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The Strongest Lines of Singly Ionized Atoms*

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ABOUT 60 years ago J. Norman Lockyer[1] called attention to the fact that certain lines appearing in arc spectra become *enhanced* in spark spectra. He believed that this change in spectrum indicated a dissociation of the radiating atom into simpler elements, but his assistant, Alfred Fowler, suspected that enhanced lines formed a new spectrum of the original element. In 1914 Fowler[2] definitely associated *enhanced lines* with *ionized atoms* of the elements. It is now known that each chemical element is characterized by Z totally different atomic spectra where Z is the atomic number, or number of extra-nuclear electrons. The first atomic spectrum (represented by I following chemical symbol) is characteristic of neutral atoms, the second spectrum (represented by II following chemical symbol) is ascribed to atoms that have lost one outer electron, and so on. The atomic energy states or spectral terms associated with these successive spectra alternate in multiplicity (being even or odd according as the number of electrons present is odd or even) but the absolute values of the states or terms increase rapidly with the stages of ionization. With each removal of a valence electron the net nuclear charge of the atom is increased by one unit, and greater energies are required to excite the charged atom. Whereas the terms in Ist spectra involve the Rydberg constant R, those of IInd spectra involve $4R$, of IIIrd spectra $9R$, etc. Ionization potentials of singly ionized atoms range from 2 to 10 (or more) times those of the corresponding neutral atoms, and the principal spectral lines of ionized atoms (except Be) have shorter wave-lengths (higher frequencies) than the chief lines of neutral atoms.

Since both arc and spark sources are commonly used in practical spectrographic analysis it is obviously of interest to compare the strongest lines of the first two spectra of the chemical elements. A year ago, I presented[3] a tentative list of the strongest lines characteristic of neutral atoms, and now I shall attempt to do the same for singly ionized atoms. At that time it was stated that there are three ways of selecting the strongest lines: (1) by accurately measuring relative intensities in atomic spectra, (2) by carefully observing the residual or most persistent line for each spectrum as the element is diluted progressively, (3) by accepting the predictions of the quantum theory of atomic spectra.

But none of these methods could give a complete answer then, and the same is true today, especially for spectra of ionized atoms. (1) Although innumerable comparisons of line

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TABLE I. *Strongest lines of the second spectra of chemical elements.*

(1) Atomic Number	(2) Element	(3) Second Ionization Potential Volts	(4) Low State cm^{-1}	(5) Electrons	(6) Low Term	(7) Excited State cm^{-1}	(8) Electrons	(9) High Term	(10) Wave-Length[1] A
1	H								
2	He	54.144	0.0	$1s$	$^2S_{0\frac{1}{2}}$	329170.	$2p$	$^2P^\circ_{1\frac{1}{2}}$	303.78
3	Li	75.258	0.0	$1s^2$	$^1S_0$	501848.	$1s2p$	$^1P^\circ_1$	199.26
4	Be	18.119	0.0	$2s$	$^2S_{0\frac{1}{2}}$	31935.4	$2p$	$^2P^\circ_{1\frac{1}{2}}$	3130.42
5	B	24.998	0.0	$2s^2$	$^1S_0$	73396.7	$2s2p$	$^1P^\circ_1$	1362.46
6	C	24.260	64.0	$2s^22p$	$^2P^\circ_{1\frac{1}{2}}$	74931.	$2s2p^2$	$^2D_{2\frac{1}{2}}$	1335.71[2]
7	N	29.443	131.3	$2s^22p^2$	$^3P_2$	92238.	$2s2p^3$	$^3D^\circ_3$	1085.74[3]
8	O	34.941	0.0	$2s^22p^3$	$^4S^\circ_{1\frac{1}{2}}$	119838.	$2s2p^4$	$^4P_{2\frac{1}{2}}$	834.47
9	F	34.81	0.0	$2s^22p^4$	$^3P_2$	164798.	$2s2p^5$	$^3P^\circ_2$	606.81
10	Ne	40.91	0.0	$2s^22p^5$	$2P^\circ_{1\frac{1}{2}}$	217053.	$2s2p^6$	$^2S_{0\frac{1}{2}}$	460.73[4]
11	Na	47.065	0.0	$2p^6$	$^1S_0$	268790.	$2p^63s$	$^1P^\circ_1$	372.07
12	Mg	14.959	0.0	$3s$	$^2S_{0\frac{1}{2}}$	35761.0	$3p$	$^2P^\circ_{1\frac{1}{2}}$	2795.53
13	Al	18.733	0.0	$3s^2$	$^1S_0$	59849.7	$3s3p$	$^1P^\circ_1$	1670.81
14	Si	16.261	287.	$3s^23p$	$^2P^\circ_{1\frac{1}{2}}$	55320.	$3s3p^2$	$^2D^\circ_{2\frac{1}{2}}$	1817.0[5]
15	P	19.59	470.3	$3s^23p^2$	$^3P_2$	65307.7	$3s3p^3$	$^3D^\circ_3$	1542.32[6]
16	S	23.3	0.0	$3s^23p^3$	$^4S^\circ_{1\frac{1}{2}}$	79394.8	$3s3p^4$	$^4P_{2\frac{1}{2}}$	1259.53[7]
17	Cl	23.70	0.0	$3s^23p^4$	$^3P_2$	93367.	$3s3p^5$	$^3P^\circ_2$	1071.05[8]
18	A	27.49	0.0	$3s^23p^5$	$^2P^\circ_{1\frac{1}{2}}$	108730.	$3s3p^6$	$^2S_{0\frac{1}{2}}$	919.78[9]
19	K	31.7	0.0	$3p^6$	$^1S_0$	166462.	$3p^64s$	$^1P^\circ_1$	600.77
20	Ca	11.82	0.0	$4s$	$^2S_{0\frac{1}{2}}$	25414.4	$4p$	$^2P^\circ_{1\frac{1}{2}}$	3933.67
21	Sc	12.8	177.6	$3d4s$	$^3D_3$	27841.2	$3d4p$	$^3F^\circ_4$	3613.84[10]
22	Ti	13.6	393.2	$3d^24s$	$^4F_{4\frac{1}{2}}$	30240.7	$3d^24p$	$^4G^\circ_{5\frac{1}{2}}$	3349.41[11]
23	V	14.1?	3162.6	$3d^34s$	$^5F_5$	35483.4	$3d^34p$	$^5G^\circ_6$	3093.11[12]
24	Cr	16.6	12498.3	$3d^44s$	$^6D_{4\frac{1}{2}}$	47753.4	$3d^44p$	$^6F^\circ_{5\frac{1}{2}}$	2835.63[13]
25	Mn	15.56	0.0	$3d^54s$	$^7S_3$	38806.5	$3d^54p$	$^7P^\circ_4$	2576.10
26	Fe	16.16	0.0	$3d^64s$	$^6D_{4\frac{1}{2}}$	41968.0	$3d^64p$	$^6F^\circ_{5\frac{1}{2}}$	2382.04
27	Co	16.9	3350.5	$3d^74s$	$^5F_5$	47078.2	$3d^74p$	$^5G^\circ_6$	2286.14[14]
28	Ni	18.4	8392.9	$3d^84s$	$^4F_{4\frac{1}{2}}$	53495.6	$3d^84p$	$^4G^\circ_{5\frac{1}{2}}$	2216.47[15]
29	Cu	20.18	21928.6	$3d^94s$	$^3D_3$	68730.8	$3d^94p$	$^3F^\circ_4$	2135.98[1]
30	Zn	17.89	0.0	$4s$	$^2S_{0\frac{1}{2}}$	49353.7	$4p$	$^2P^\circ_{1\frac{1}{2}}$	2025.51
31	Ga	20.43	0.0	$4s^2$	$^1S_0$	70700.	$4s4p$	$^1P^\circ_1$	1414.44
32	Ge	16.	1768.	$4s^24p$	$^2P^\circ_{1\frac{1}{2}}$	62402.	$4s^25s$	$^2S_0$	1649.26[17]
33	As	20.1	2540.	$4s^24p^2$	$^3P_2$	81507.	$4s^24p5s$	$^3P^\circ_2$	1266.36[18]
34	Se	21.5	0.0	$4s^24p^3$	$^4S^\circ_{1\frac{1}{2}}$	83876.7	$4s4p^4$	$^4P_{2\frac{1}{2}}$	1192.29[19]
35	Br	19.1	0.0	$4s^24p^4$	$^3P_2$	98476.4	$4s^24p^35s$	$^3S^\circ_1$	1015.42[20]
36	Kr	24.47	0.0	$4s^24p^5$	$^2P^\circ_{1\frac{1}{2}}$	109002.	$4s4p^6$	$^2S_{0\frac{1}{2}}$	917.43[21]
37	Rb	27.3	0.0	$4p^6$	$^1S_0$	134875.	$4p^65s$	$^2P^\circ_1$	741.4
38	Sr	10.98	0.0	$5s$	$^2S_{0\frac{1}{2}}$	24516.7	$5p$	$^2P^\circ_{1\frac{1}{2}}$	4077.71
39	Y	12.3	1449.9	$4d5s$	$^3D_3$	28394.3	$4d5p$	$^3F^\circ_4$	3710.29[22]
40	Zr	13.97	1322.9	$4d^25s$	$^4F_{4\frac{1}{2}}$	30795.7	$4d^25p$	$^4G^\circ_{5\frac{1}{2}}$	3391.98[23]
41	Cb		4146.0	$4d^35s$	$^5F_5$	36455.5	$4d^35p$	$^5G^\circ_6$	3094.18[24]
42	Mo		13460.7	$4d^45s$	$^6D_{4\frac{1}{2}}$	48959.6	$4d^45p$	$^6F^\circ_{5\frac{1}{2}}$	2816.15[25]
43	Ma								
44	Ru		9151.5	$4d^55s$	$^6D_{4\frac{1}{2}}$	50758.2	$4d^55p$	$^6F^\circ_{5\frac{1}{2}}$	2402.72[26]
45	Rh		16885.0	$4d^75s$	$^5F_5$	59702.	$4d^75p$	$^5G^\circ_6$	2334.77[27]
46	Pd	19.8	25081.0	$4d^85s$	$^4F_{4\frac{1}{2}}$	68611.5	$4d^85p$	$^4G^\circ_{5\frac{1}{2}}$	2296.53[28]
47	Ag	21.9	39163.9	$4d^95s$	$^3D_3$	83665.2	$4d^95p$	$^3F^\circ_4$	2246.41[29]
48	Cd	16.84	0.0	$5s$	$^2S_{0\frac{1}{2}}$	46618.5	$5p$	$^2P^\circ_{1\frac{1}{2}}$	2144.38
49	In	18.79	0.0	$5s^2$	$^1S_0$	63036.	$5s5p$	$^1P^\circ_1$	1586.4
50	Sn	14.5	0.0	$5s^25p$	$^2P^\circ_{0\frac{1}{2}}$	46463.	$5s5p^2$	$^4P_{1\frac{1}{2}}$	2152.22[30]
51	Sb	18.	5659.	$5s^25p^2$	$^3P_2$	67887.	$5s5p^3$	$^3D^\circ_3$	1606.98[31]
52	Te								
53	I	19.4	0.0	$5s^25p^4$	$^3P_2$	81040.	$5s^25p^26s$	$^5S^\circ_2$	1233.97[32]
54	Xe	21.1	0.0	$5s^25p^5$	$^2P^\circ_{1\frac{1}{2}}$	90873.8	$5s5p^6$	$^2S_{0\frac{1}{2}}$	1100.42[33]
55	Cs	23.4	0.0	$5p^6$	$^1S_0$	107905.	$5p^56s$	$^3P^\circ_1$?	926.75
56	Ba	9.96	0.0	$6s$	$^2S_{0\frac{1}{2}}$	21953.0	$6p$	$^2P^\circ_{1\frac{1}{2}}$	4554.04
57	La	11.38	3250.4	$5d6s$	$^3D_3$	28565.4	$5d6p$	$^3F^\circ_4$	3949.10[34]
58	Ce	12.3?	3113.6	$4f^26s$	$^4H_{4\frac{1}{2}}$	26992.6	$4f^26p$	$^4I^\circ_{7\frac{1}{2}}$	4186.60[35]
59	Pr		1649.0	$4f^36s$	$^5I^\circ_4$	25569.1	$4f^36p$	$^5K_7$	4179.42[36]
60	Nd		0.0	$4f^46s$	$^6I_{3\frac{1}{2}}$	23230.0	$4f^46p$	$^6K^\circ_{4\frac{1}{2}}$	4303.57[37]
61	—	—	—	—	—	—	—	—	—
62	Sm		3909.6	$4f^56s$	$^8F_{6\frac{1}{2}}$	31926.4	$4f^56p$	$^8G^\circ_{7\frac{1}{2}}$?	3568.27[38]
63	Eu	11.4	0.0	$4f^76s$	$^9S_4$	23774.3	$4f^76p$	$^9P_5$	4205.05[39]
64	Gd								
65	Tb								
66	Dy								
67	Ho								
68	Er								

TABLE 1. (*Continued.*)

(1) Atomic Number	(2) Element	(3) Second Ionization Potential Volts	(4) Low State cm^{-1}	(5) Electrons	(6) Low Term	(7) Excited State cm^{-1}	(8) Electrons	(9) High Term	(10) Wave-Length[1] A
69	Tm		0.0	$4f^{13}6s$	$^3F^\circ_4$	25980.0	$4f^{13}6p$	$^3F_4$?	3848.02[40]
70	Yb	12.05	0.0	$6s$	$^2S_{0\frac{1}{2}}$	27061.9	$6p$	$^2P^\circ_{0\frac{1}{2}}$	3694.20[41]
71	Lu		0.0	$6s^2$	$^1S_0$	38223.2	$6s6p$	$^1P_1$	2615.43[42]
72	Hf	14.8	8361.8	$5d^26s$	$^4F_{4\frac{1}{2}}$	46209.1	$5d^26p$	$^4G^\circ_{5\frac{1}{2}}$	2641.41[43]
73	Ta								
74	W		6147.1	$5d^46s$	$^6D_{4\frac{1}{2}}$	51495.0	$5d^46p$	$^6F^\circ_{5\frac{1}{2}}$?	2204.49[44]
75	Re								
76	Os								
77	Ir								
78	Pt	18.47	4786.6	$5d^86s$	$^4F_{4\frac{1}{2}}$	61058.6	$5d^86p$	$^4G^\circ_{5\frac{1}{2}}$	1777.09[45]
79	Au	20.0	15039.0	$5d^{9}6s$	$^3D_3$	72494.8	$4d^{9}6p$	$^3F^\circ_4$	1740.47[46]
80	Hg	18.672	0.0	$6s$	$^2S_{0\frac{1}{2}}$	60608.	$6p$	$^2P^\circ_{1\frac{1}{2}}$	1649.96
81	Tl	20.33	0.0	$6s^2$	$^1S_0$	52393.	$6s6p$	$^3P^\circ_1$	1908.64[47]
82	Pb	14.96	0.0	$6s^26p$	$^2P^\circ_{0\frac{1}{2}}$	57911.	$6s6p^2$	$^4P_{0\frac{1}{2}}$	1726.75[48]
83	Bi	16.6	17025.	$6s^26p^2$	$^3P_2$	69590.	$6s^26p7s$	$^3P^\circ_1$	1902.41[49]
84	Po								
85	—	—	—	—	—	—	—	—	—
86	Rn								
87	—	—	—	—	—	—	—	—	—
88	Ra	10.10	0.0	$7s$	$^2S_{0\frac{1}{2}}$	26208.9	$7p$	$^2P^\circ_{1\frac{1}{2}}$	3814.42[50]
89	Ac								
90	Th								
91	Pa								
92	U								

[1] Data in Table I are taken from *Atomic Energy States* by Bacher and Goudsmit (McGraw-Hill, New York, 1932) except where notes indicate more recent authorities. Wave-lengths greater than 2000A are taken from *M.I.T. Wavelength Tables* (John Wiley, New York, 1939); shorter than 2000A from *Tabelle der Hauptlinien der Linienspektren aller Elemente* (Kayser-Ritschl, Julius Springer, Berlin, 1939).

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intensities in spark spectrograms are made daily in routine spectrochemical analysis, the measured lines often belong to neutral atoms, and deliberate attempts to determine intensity ratios of enhanced lines are extremely rare. (2) Residual or persistent lines observed in the spectra of condensed spark discharges have been published by Hartley,[4] by Pollok,[5] by deGramont,[6] and by Löwe,[7] but none of these investigators except Löwe distinguished between successive spectra, and their results apply mainly to neutral atoms because the strongest lines of ionized atoms often occur in the extreme ultraviolet. (3) Thus far relative intensities of lines originating in any one configuration of electrons are theoretically known, and then only in cases of ideal coupling (pure *ls* or *jj*). Of special interest is a comparison of the strongest line from $d^n s^2 - d^n sp$ with the strongest line from $d^{n+1}s - d^{n+1}p$, but this theoretical problem has not been solved. Furthermore, on account of greater nuclear charges, the spectra of ionized atoms generally exhibit wider fine structure, and more overlapping and mutual perturbation of quantum states so that the simple rules for line intensities do not always apply. Finally, it must be admitted that our knowledge of the facts and properties of spectra of ionized atoms is less complete than for neutral atoms. In view of these circumstances this attempt to select the strongest lines belonging to singly ionized atoms may be criticized as premature. However, a sufficient number of IInd spectra have now been described and analyzed to permit the deduction of some general principles, and the success of such generalizations in explaining certain empirical observations may perhaps justify the writing of this paper.

Data for the strongest lines of singly ionized atoms are presented in Table I, in which successive columns contain (1) atomic number, (2) chemical symbol, (3) second ionization potential, (4) low energy state, (5) electrons, (6) low spectral term, (7) excited energy state, (8) electrons (9) high spectral term, and (10) observed wave-length of the strongest line. Footnotes to the table are indicated by small numbers in the last column.

The ionization potentials (3) are given in volts; they are proportional to the minimum energies required to remove a second electron from each atom after the atom has been once ionized.[8] Second ionization-potential values range from 9.96 v (Ba) to 75.258 v (Li) and, like first ionization potentials, they show maxima for closed shells and minima for atoms beginning new shells. For once-ionized atoms these maxima and minima occur at one unit larger atomic number than for neutral atoms, and the general properties of spectral structure are likewise shifted (*displacement law*). Ionized atoms with normal configurations of s^2 electrons (e.g., B, Al, Ga, In) are generally very stable, and when two to six p electrons are also present the stability tends to increase until maxima are periodically reached with ionized alkalis (Na, K, Rb, Cs). In order to excite such atoms either the stable s^2 subgroup must be disrupted or a p electron must be changed to s with increased total quantum number (next shell). In either case the excited states are very high and the strongest radiated lines lie in the extreme ultraviolet (<2000A). However, ionic configurations containing only one s electron (Be, Mg, Ca, Zn, Sr, Cd, Ba, Yb) or one such electron combined with type d (21 Sc to 29 Cu, 39 Y to 47 Ag, 72 Hf to 79 Au), or with type f (58 Ce to 70 Yb) electrons have relatively low stability and very large transition probability because in each case the s electron is easily converted to p without leaving its shell. This simple $s \rightleftarrows p$ transition generally produces lines of outstanding intensity and longer wave-length, and therefore the 40± elements just mentioned are the only ones yielding strongest lines in the range of routine observation (i.e., >2000A).

The atomic (ionic) energy states producing the strongest lines are displayed in columns 4 and 7, the corresponding electron configurations and spectral term symbols appear respectively in columns 5 and 8, and 6 and 9. The energy values are expressed in reciprocal centimeters (8106 $cm^{-1} = 1$ volt); they are relative to 0.0 cm^{-1} for the lowest energy (normal state) of singly

[4] W. N. Hartley, Phil. Trans. Roy. Soc. **175**, 327 (1884).
[5] J. H. Pollok, Proc. Roy. Dublin Soc. **15**, 184 (1907).
[6] A. deGramont, Comptes rendus **171**, 1106 (1920).
[7] F. Löwe, *Atlas der letzten Linien der wichtigsten Elemente* (T. Steinkopff, Dresden, 1928).

[8] Ionization potentials are quoted from a paper by J. C. Boyce, Rev. Mod. Phys. **13**, 1 (1941).

ionized atoms. A majority of the strongest lines of ionized atoms involve the normal state when the spectral term (6) is single valued or when polyfold terms are "inverted" (level with largest J has lowest energy), but there are many instances where the strongest line ends on a metastable state. These exceptions are of two kinds: (1) those in which the fine structure of the term is "normal" (level with smallest J has lowest energy as in C, N, Si, P, Sc, Ti, V, etc.), and (2) those in which a metastable level arising from the configuration containing a single s electron competes successfully with lower levels from alternative configurations (Cr, Co, Ni, Cu, Mo, Ru, etc.).

Speaking generally for spectra arising from transitions between families of polyfold levels, the strongest lines result from transitions between levels with largest L and J values, but for ionized atoms especially, due to coarser fine structure and to mutual perturbation of states, this simple intensity rule is sometimes violated. Anomalous intensities occur in many spark multiplets (especially in spectra of the rare-earth elements) but at present these are indicated only by visual estimates since no precise measurements of relative intensities in complex IInd spectra have been made, nor has the quantum theory of spectral line intensities been developed sufficiently to predict these intensities. The strongest lines (10) have been selected mainly from relative intensity estimates of the authorities cited. Not all intensity estimates or analyses of spectral structure are equally reliable or final but there is no good reason to doubt the general correctness of Table I.

Notwithstanding the incompleteness of our information concerning IInd spectra we can nevertheless hazard some conclusions as to general principles. It appears to be a general rule for singly ionized atoms (as well as for neutral atoms) that the strongest lines result from transitions between s and p types of valence electrons, that is, from orbital momentum changes from 0 to 1. Ionized atoms that possess only one valence s-type electron are least stable and will undoubtedly exhibit the highest absolute sensitivity. When other types of valence electrons (p, d, f) are also present the following statements appear to apply to the strongest lines of ionized atoms: Electron configurations s^2 and s^2p^n ($n=1$ to 6) have high stability resulting in high frequency (extreme ultraviolet) radiation of strongest lines. Configurations of one s electron and one or more of type d or f have intermediate stability. These yield ground states or metastable ones that are easily excited by converting s to p, and strong lines are emitted when p returns to s. Nearly all ionized atoms containing a single s electron emit strongest lines with wave-lengths greater than 2000A and when f-type electrons are present the strongest lines probably have wave-lengths greater than 3500A.

Of what interest to practical spectrographers are the above facts and generalizations about ionized atoms? Every experienced spectrographer knows that many chemical elements emit both Ist and IInd spectra in arcs or sparks operated at atmospheric pressure. For example, every one has seen 3130 Be II, 2795 Mg II, 3933 Ca II, 4077 Sr II, 4554 Ba II in arc spectrograms and it is not improbable that 2795 Mg II has appeared stronger than 2852 Mg I, or 3933 Ca II stronger than 4226 Ca I. It is common experience also that the relative intensities of Ist and IInd spectra in both arcs and sparks are functions of the operating conditions in the light sources, and also of the part of the source from which light is taken. Sometimes even higher stages of spectra (III, IV, etc.) are observed in conventional light sources (but for the identification of such lines one should consult the Kayser-Ritschl *Hauptlinien* rather than the *M.I.T. Wavelength Tables*). Some practical spectrographers have observed that many elements exhibit a higher absolute sensitivity in the arc than in the spark, and that rare-earth elements are insensitive in the ultraviolet. Explanations of such experiences and observations should be sought in properties of the atoms and of the light sources.

Excitation (and ionization) in the light column of an electric arc (or spark) at atmospheric pressure is mainly a thermal mechanism of atomic collisions with electrons in vapors at temperatures exceeding 6000°K. It has been shown[9] that the electron temperature and the gas temperature differ by less than one percent

[9] R. Mannkopff, Zeits. f. Physik **86**, 161 (1933).

and that temperature equilibrium is practically complete in the arc column. However, the ionization limits in arcs (and sparks) are not set by the prevailing gas temperatures but by the cathode fall of potential. When the electrodes of a d.c. arc are accurately focused on the slit of a stigmatic spectrograph it is commonly observed that IInd spectra are enhanced at the cathode and some elements even exhibit IIIrd spectrum lines at the cathode. When high voltage condensed sparks are similarly examined the light column is found to consist of Ist and IInd spectra while IIIrd and IVth (or higher) spectra appear enhanced or only at the electrodes. The pure spectroscopist has long made use of these phenomena to identify the spectral lines belonging to successive stages of ionization.

The fall of potential in metallic arcs in air is of the order of 30 volts, while in high voltage condensed sparks the effective drop is of the order of 50 volts. That a considerable portion of this potential drop occurs in the immediate vicinity of the cathode, has been determined by electrical measurements in the d.c. arc,[10] besides being indicated by spectroscopic observations. That similar conditions prevail in high voltage a.c. arcs and in condensed sparks may be concluded from the enhancement or excitation at the electrodes of lines from ionized or multiply ionized atoms. The total light from conventional sources is thus a mixture of successive spectra among which the lower ones have mainly thermal and the higher ones chiefly electrical origin,[11] and although the relative intensities of lines in any particular spectrum are fairly independent of conditions the relative intensities of successive spectra will show large differences as functions of excitation conditions and of various portions of the light source or methods of illuminating the spectrograph.

First-ionization potentials are now known for 76 elements and second-ionization potentials have been determined (or estimated) for 61 elements. The first range from 3.87 v for Cs to 24.465 v for He, while the second range from 9.96 v for Ba to 75.258 v for Li. Among the 70 elements regularly tested spectrographically none have first-ionization potentials exceeding 11.2 volts and only 4 have second-ionization potentials exceeding 25 volts. The latter are the ionized alkali atoms which, having gained a unit of nuclear charge, are more stable than the analogous noble gas shells. Spectra of the most stable ions are not observed in conventional light sources either because they are not excited or because they occur in the range of vacuum spectroscopy. In such cases the practical spectrographer looks for Ist spectrum lines even in spark spectrograms because he knows or hopes that some ionized atoms return to the neutral state in spite of high temperature or applied potential.

The apparent abundance of certain neutral atoms in sparks and of certain ionized atoms in arcs is magnified when such atoms have a single valence electron of s type because the $s \rightleftarrows p$ transition always yields lines of extraordinary intensity. For example, the strongest Ca I line (4226A) arises from the $s^2 \rightleftarrows sp$ transition but the strongest Ca II line (3933A) represents $s \rightleftarrows p$. In the first case the relatively stable s^2 subgroup must be broken up and one of the electrons energized to a p state, while in the second case, after ionization, the remaining s electron is easily converted to the p state. In general, atoms with a single s electron in the normal state are many times more sensitive spectrochemically than those with s^2, and consequently a small number of the former may produce a stronger line than a much larger number of the latter. This may be the main factor in explaining the abnormal intensity of IInd spectrum lines of alkaline earths in arc spectra, especially when light from the cathode enters the spectrograph. It appears that this also accounts in large part for the strength of IInd spectrum lines in the commonly observed range of arc spectra of elements in the long periods which include d- and f-type electrons. Ionized atoms 21 Sc to 29 Cu and 39 Y to 47 Ag have electron configurations of one s electron combined with one to nine d electrons and the strongest line is easily obtained by exciting s to p. Even in cases where the $d^n s$ configuration gives metastable rather than ground states, the transition $d^n s \rightleftarrows d^n p$ seems to be preferred unless the elevation of the metastable state exceeds several volts.

Although our knowledge of the structure of

[10] G. H. Fett, J. App. Phys. **12**, 436 (1941).
[11] H. Witte, Zeits. f. Physik **88**, 415 (1934).

rare-earth spectra is still far from complete, the available evidence indicates that the singly ionized elements 58 Ce to 70 Yb have ground (or low metastable) states resulting from a single s electron combined with two to fourteen f electrons, and consequently show strong lines arising from $s \rightleftarrows p$ transitions. The strongest lines of ionized rare earths are expected to lie between 3500A and 5000A, and reported inability to detect traces of rare earths in the shorter ultraviolet is thus explained. Because rare earths are easily ionized it is possible that their strongest IInd spectrum lines will surpass in intensity the strongest Ist spectrum lines in ordinary arcs, and also probable that their absolute sensitivity will be reduced in sources where higher temperatures and greater potential gradients favor multiple ionization. The relative insensitiveness of the high frequency spark discharge used in microanalysis is undoubtedly due to multiple ionization since the potential drop across the gap is very large (2000 volts).[12]

[12] William M. Murray, Jr., Briggs Gettys, and Samuel E. Q. Ashley, J. Opt. Soc. Am. **31**, 433 (1941).

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Spectrochemical Analysis of Duralumin Type Alloys*

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Introduction

THE routine spectrographic analysis of aluminum alloys has undergone rapid development during the last few years. The rapidly increasing production of aluminum and the increasing demand for more rigid control of alloy compositions have combined to establish conditions favorable for the introduction of the spectrograph as a routine analytical tool. In the Aluminum Company of America, some of the routine analytical laboratories analyze an average of about 500 metal samples per day, with as many as nine determinations per sample in some cases. To handle this type of work, we now have fifteen spectrographic laboratories either operating or under installation, and are considering several more. By the end of this year we expect to handle about 80 percent of the analytical control work on aluminum alloys spectrographically, with economy and speed which could not be approached by wet chemical methods.

The determinations regularly made on a routine basis in these laboratories include silicon, iron, copper manganese, magnesium, zinc, lead, chromium, tin, titanium, and bismuth. Since, in most cases, several of these determinations are made simultaneously, the method employed on a particular sample is necessarily a compromise among the optimum working conditions for the various elements to be determined. Virtually all of our routine quantitative tests are made by the use of spark spectra. Hence, the general techniques employed and the problems encountered in determining various elements are very similar, and a detailed consideration of any one determination will serve to present a general picture of our spectrographic work in its present status. We have selected the determination of copper in the range of 2.5 to 5.0 percent for this discussion for two main reasons. First, the problems encountered in this determination are typical of those met with, to a greater or less degree, in most determinations made on aluminum alloys; and second, spectro-analysts in general seem to regard this determination as particularly difficult.

The Spectrograph

The type of spectrograph employed in a particular laboratory is, of course, determined by the nature and volume of work to be carried out. In our research laboratories, where maxi-

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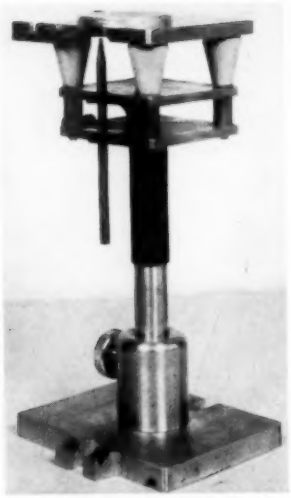

FIG 1. Spark stand.

mum flexibility, photographic speed, and quality of spectra are essential, a Gaertner L254 two-prism spectrograph is used. In our routine laboratories, three Bausch and Lomb large Littrow spectrographs and one large Hilger Littrow instrument are in use, and ten Dietert-Applied Research Laboratories grating spectrographs will be employed.

DENSITOMETERS

We are using two types of densitometers in our laboratories, the choice between the two types being determined by the type of spectrograph employed. The laboratories using Littrow type prism instruments are equipped with Leeds and Northrup recording microphotometers, and our research laboratories use a Leeds and Northrup Speedomax Recorder in conjunction with a microphotometer unit made in the shop at the laboratories. The latter instrument is a modification of an apparatus made before the Leeds and Northrup microphotometer was developed and is virtually equivalent to the Leeds and Northrup instrument. The laboratories using grating spectrographs made by Dietert-Applied Research Laboratories are using combination comparator-densitometers made by the same manufacturer. These instruments are particularly well suited to the handling of the 35-millimeter film used on this type of spectrograph, and, combining as they do the functions of a comparator and a densitometer, are somewhat more foolproof for inexperienced personnel than those types of densitometers which lack wave-length guides, visible during the process of measurement.

EXCITATION SOURCES

While all of our laboratories are equipped with d.c. arc source units and some with high voltage a.c. arc apparatus, virtually all of our metallurgical analysis is carried out by means of spark spectra. In selecting spark sources, we found at the outset that there was no completely satisfactory spark source available commercially. Accordingly, we undertook to build excitation units in three of our laboratories. These units have proved individually satisfactory in the applications for which they were designed. Recently, however, there has developed a need for rigid standardization of equipment among our various laboratories. This need, coupled with the improvement in commercially available spark apparatus, has caused us to turn to ready-built spark sources. For routine spectrographic work, we have now standardized on the "Heavy Duty" spark unit manufactured by Dietert-Applied Research Laboratories. This apparatus is built around the conventional type of spark circuit, consisting of a 35,000-volt transformer with a bank of condensers connected across the secondary, and a synchronous interrupter and variable inductance in series with the spark gap. The unit is compact and fairly rugged, and the adjustments and controls are simple and well arranged. With a few minor modifications, we have found this apparatus very satisfactory in our routine laboratories.

SPARK STAND

The type of spark stand employed in all of our laboratories doing metallurgical analysis is shown in Fig. 1. This stand was designed to handle flat cast sample plates of the type ordinarily used in most of our routine work, but can be used for any type of sample having a flat surface large enough to cover the opening in the supporting plate. Most of our routine quantitative analyses are made by using a spark discharge between a precisely shaped graphite rod

and a machined flat surface of the sample. Such an arrangement is shown in the illustration. These spark stands are equipped with automatic gages which adjust the position of the graphite rod to give the correct electrode spacing, and in some cases with auxiliary equipment to facilitate the sparking of rod electrodes, small rivets, or fabricated articles of odd shapes. We have found this type of spark stand particularly well suited to our work. Its chief advantages lie in the high accuracy and reproducibility of spark dimensions and optical alignment, the elimination of overheating of samples by contact with the heavy aluminum supporting plate, the ability to handle samples of widely varying sizes and shapes with a minimum of sample preparation, and the elimination of the necessity of any adjustment of spark position during a series of tests.

Other Equipment

Numerous other pieces of equipment and small gadgets are needed in these routine laboratories. Included among these are the thermostatically controlled developing machines, washers and driers for films and plates, lathes for facing samples, devices for numbering plates or films, projectors for viewing plates, and devices for shaping graphite electrodes.

Electrical and Optical Conditions

The electrical and optical conditions used for the copper determination depend to a large degree on the other elements to be determined simultaneously and on the type of spectrograph used. On most alloys of the Duralumin type, copper, magnesium, manganese, iron, and silicon are regularly determined on the same spectrogram. The working conditions employed are largely determined by the percentages of magnesium and silicon.

The principal effect of magnesium is to produce a disproportionately large reduction in the intensity of the other lines in the spectrum. This effect is shown in Fig. 2, where the relationships between magnesium content and relative intensity of copper and aluminum lines, and between magnesium content and the Cu 2370/Al 2369 intensity ratio are shown for a particular set of excitation conditions. The decrease in general intensity produced by varying magnesium content makes it necessary to use different electrical or optical conditions for alloys containing widely different magnesium contents and necessitates corrections in intensity ratio-percentage relationships for all elements other than magnesium when the magnesium content varies over a wide range. Similar mutual effects of one element on the behavior of another are to be expected in most analyses. Usually the effects are less pronounced than in the case of magnesium.

In certain aluminum-copper alloys where it is necessary to determine small amounts of silicon, lead, or zinc, it is necessary to use high secondary inductance values. The addition of inductance alters the intensity relationships between copper and aluminum lines and necessitates separate working curves for use at different inductance values.

Having selected a set of electrical conditions which will give spectrum lines of satisfactory relative intensities for the alloy under test, the next step is, of course, to bring the absolute intensities within a favorable range for photography. Since we use the same type of emulsion on all work of this kind and since we have standardized on ten-second exposures, the adjustment of total intensity must be accomplished either optically or electrically. Of the optical methods, the simplest and most generally satisfactory, when applicable, is to alter the distance from spark to spectrograph. Our

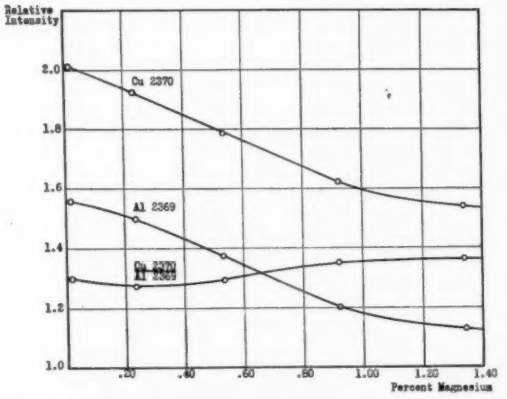

Fig. 2. The effect of magnesium on copper and aluminum intensities in spark spectra of Duralumin type alloys.

Gaertner, Bausch and Lomb, and Hilger instruments are fitted with optical benches providing a movement of three feet or more. Hence, with these instruments we can vary intensity at the slit over a wide range without changing electrical conditions or resorting to filters, reducing sectors, or other auxiliary apparatus. The Dietert-Applied Research Laboratories instrument has a much shorter optical bench and the total movement of the spark is only about one foot. Hence, the range of intensity adjustment obtainable by movement along the optical bench is relatively small with this instrument. Other optical variables include slit width, variable apertures in front of grating or collimator, filters, fine-mesh screens, and rotating sectors. We have found it undesirable to change slit width frequently, since this adjustment is difficult to reproduce on any of the spectrographs we have used. Collimator and grating apertures are useful variables, but on most spectrographs this adjustment is step-wise in rather broad steps. Filters, mesh screens, and similar means of reducing intensity are often a nuisance in high speed routine work and do not provide a continuous non-step-wise adjustment. Rotating sectors may be used satisfactorily with spark spectra, provided they are run at a constant speed at which no stroboscopic effect is obtained. Unfortunately, this requirement is not met in the sectors regularly furnished by the spectrograph manufacturers.

Although it is common practice to use electrical variables to adjust total intensity of the spark, great care must be taken to avoid introducing undesirable effects into the spark discharge. When one electrical variable is altered it is generally necessary to alter other variables in order to maintain a reproducible spark. With ARL-Dietert spark units, transformer power and condenser capacity may be used at four different values, producing four widely different intensity levels. To obtain spark intensities lying between those obtained at successive power settings, we can vary either the positions of the interrupter points or the secondary inductance. Variation in the self-inductance of the spark circuit greatly alters the intensity relationships between certain lines, particularly when they are produced at different ionization states, and the amount of self-inductance used in the analysis of copper-bearing aluminum alloys is usually predetermined by the range of silicon percentages expected. Self-inductance is, therefore, rarely used as an adjustment of total intensity. Rotation of the stationary interrupter points changes the voltage applied to the electrodes at the instant of discharge, since it changes the time of discharge with respect to the voltage wave. The angle over which the interrupter points may be moved without impairing the quality of the spark is rather limited. If the points are set at too low a voltage the spark fails to fire every half-cycle, and if the voltage is too high there is a tendency towards an occasional extra discharge. In either case the spark becomes too erratic for quantitative use if the stationary points are rotated too far. In quantitative work the total range over which the time of discharge can be varied with respect to the voltage wave is usually less than one-fourth of a cycle.

In general, we prefer to use optical methods for regulating intensity, since these methods do not appreciably affect the relationships between intensity ratios and percent constituent. In routine applications, where the flexibility of the apparatus is insufficient for convenient adjustment by such methods, we often vary our electrical conditions. In such cases, of course, extensive preliminary experimental work is necessary to determine over what range the electrical adjustments may be varied without altering percentage-intensity ratio relationships.

Preparation of Spectrograms

In all of our routine quantitative work we are using a machined surface of the sample as the upper electrode and a tapered graphite rod having a 2-mm flat circular tip as the lower electrode. The gap is always 3 mm and a freshly prepared graphite electrode is used for each test. A pre-sparking period of 20 seconds is employed to permit the spark to approach some semblance of an equilibrium condition and to remove any surface impurities which may originate from machining or handling the electrodes. Ten-second exposures are employed for all copper determinations and for most other tests.

With prism spectrographs, we are using Eastman Spectrum Analysis No. 1 plates, and with

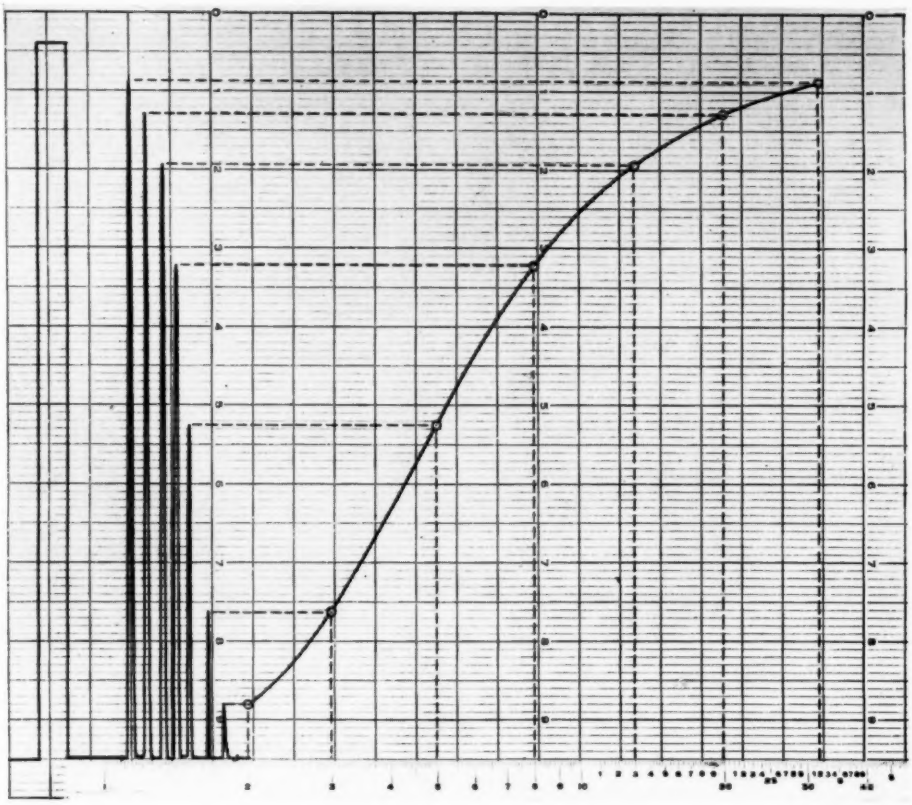

FIG. 3. Emulsion calibration curve.

grating instruments we use a film bearing the same type of emulsion. All plates and films are developed three minutes in Eastman Formula D-19 developer at 65°C. Thermostatically controlled developing machines mechanically agitating the developer tray, and suitable apparatus for rapidly washing, cleaning, and drying plates are provided in all installations.

PREPARATION OF STEPPED SPECTROGRAMS

The first step in the quantitative interpretation of a spectrogram is the establishment of the relationship between intensity and image density at constant exposure time. To do this we use stepped spectrograms prepared by the use of an iron arc or spark and a step sector. The step sector used is rotated at a speed sufficient to eliminate any intermittency effect so that successive stepped spectrograms can be treated as exposures of equal time but varying intensity. The ratio between steps varies among different laboratories from 1.5 to 2.0 and the ratio of minimum to maximum steps from 8 to 34. The optical adjustment must be such that the face for the sector is illuminated uniformly over the area in front of the slit. This is easily accomplished by the use of a suitable lens focusing on the grating or collimator lens, depending on the type of spectrograph employed.

While we are able to obtain perfectly satisfactory emulsion calibrations by the use of spark spectra, great care must be taken to avoid stroboscopic effects. Although commercially available step sectors are powered by motors equipped with rheostat speed controls, this type of control is never sufficiently precise to maintain a speed such that no stroboscopic effect is produced. Using such apparatus, we have found it possible

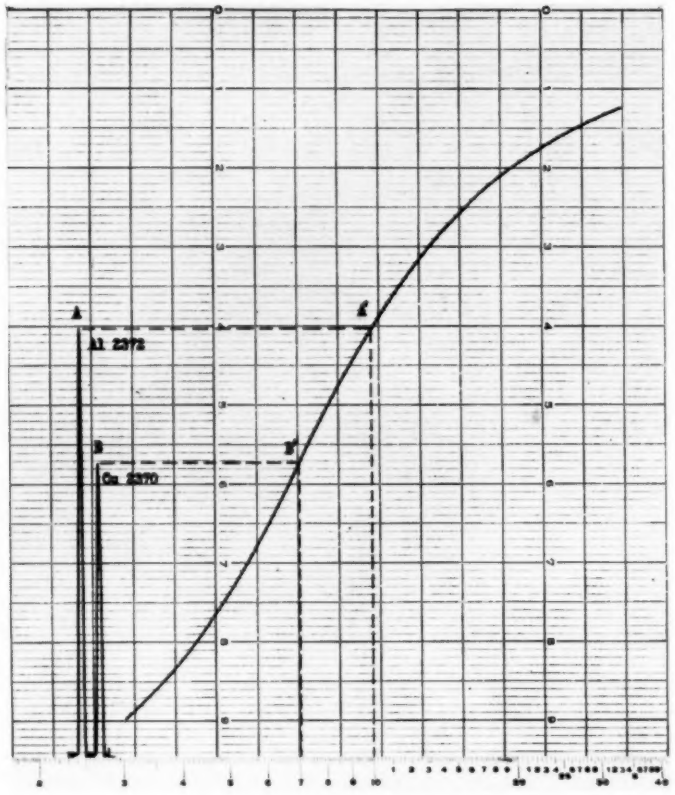

FIG. 4. Calculation of intensity ratios.

to obtain accurate calibration data by taking our exposure at changing sector speed at a predetermined time interval after a stroboscopic image is observed on the sector face. In such cases, several stepped spectrograms are usually prepared and checked against one another for possible errors. The most satisfactory method we have found for producing calibration spectra from a spark source is by the use of a conventional type of sector disk run at constant speed by a synchronous motor with a speed reducer selected to give a speed at which no stroboscopic effect is possible. We expect to modify the sector apparatus in some of our routine laboratories along these lines.

Of course, the simplest means of avoiding stroboscopic effects is by the use of a non-intermittent source, such as the d.c. arc, and some of our laboratories are regularly using arc spectra for emulsion calibration. Unfortunately, this is not always convenient because of difficulties encountered in adjusting and maintaining the position of the arc. On our large prism spectrographs, where the distance from arc to sector can be as great as three feet, the position of the arc is not very critical and can be controlled sufficiently to provide uniform slit illumination from top to bottom. On the grating instruments, however, with their short optical benches, the arc is relatively close to the sector and any wandering of the arc is more serious. We have been unable, so far, consistently to adjust arc position with sufficient precision in routine work to use arc sources for film calibration on these instruments. Of course, the difficulties involved in taking stepped spark spectrograms with standard commercial apparatus are not prohibitive, since it is necessary to determine

calibration curves only once for a given emulsion batch and the necessity for taking several stepped spectra to detect stroboscopic effects loses significance in view of the fact that it is generally desirable to base a calibration curve on more than one spectrogram, even under the best conditions, in order to average out errors in densitometry and possible local effects in the emulsions.

Preparation of Calibration Curves

In routine work the mechanics of preparation and use of working curves depend to a degree on the type of apparatus used. The use of a recording microphotometer, such as the Leeds and Northrup instrument, has certain definite advantages, particularly in handling large numbers of samples where high speed is desirable since the numerical data are required and the manipulations of calculation are somewhat simplified.

Figure 3 shows a typical densitometer chart prepared on a Leeds and Northrup microphotometer for the purpose of establishing the calibration curve for an emulsion. This chart is mounted on a calculating board equipped with a vertically movable T-square slotted to hold a logarithmically inscribed rule. The calibration curve is plotted by using the actual heights of the densitometer peaks as ordinates and the known relative intensities as abscissae. Keeping the rule at fixed position from right to left, it is moved vertically until the edge of the rule intersects the deflection peak corresponding to a particular relative intensity. A point is then marked on the chart along the edge of the rule at the scale reading corresponding to the relative intensity. The relative intensities (relative sector apertures) used in constructing the calibration curve shown were 32, 20, 13, 8, 5, 3, and 2. Figure 3 is an actual photograph of a chart actually made on a Speedomax Recorder actuated by a densitometer similar to the standard Leeds and Northrup instrument. The chart, as photographed, was mounted on a calculating board, and the logarithmic scale used in plotting is shown at the bottom of the chart. In practice these curves are drawn with India ink and mounted semi-permanently on the calculating board. Densitometer charts to be analyzed are superimposed on it. These charts are made on paper of sufficient translucency for use in this way.

Interpretation of Sample Spectra

In Fig. 4 is shown a chart bearing densitometer tracings representing Cu 2370 and Al 2369 in a spectrum of a 4 percent copper alloy. Superimposed on this chart is the calibration curve from Fig. 3. This curve and the chart bearing the sample deflections must be placed at the correct vertical position with respect to the densitometer chart, but may be at any convenient position from right to left. Now if we use the same log scale employed in preparing the calibration curve, and if we place it at a height such that its edge intersects the peak for the aluminum, read the scale at its intersection with the calibration curve, then move the scale vertically until its edge intersects the copper peak and again read the scale at its intersection with the calibration curve, the two readings we have taken will be directly proportional to the intensities of the light striking the emulsion at the two wave-lengths. Obviously, if, when we lined up the scale with the aluminum peak, we had moved the rule horizontally until the calibration curve intersected the scale at unity and then moved it vertically to the copper peak, the scale reading at its intersection with the calibration curve would then give the ratio of the intensities of the copper and aluminum lines. Now, since this ratio is determined by the percent

Table I. *Reproducibility tests.—Successive analyses of the same sample.*

Test	Si	Fe	Cu	Mn	Mg
1	0.43%	0.44%	3.98%	0.67%	0.60%
2	.43	.41	3.82	.66	.61
3	.43	.42	3.89	.67	.61
4	.44	.46	4.05	.68	.61
5	.43	.44	4.00	.66	.60
6	.44	.42	4.05	.63	.60
7	.44	.40	4.08	.63	.62
8	.42	.40	4.14	.63	.62
9	.41	.40	3.89	.63	.59
10	.42	.40	4.08	.65	.60
Chemical analysis	0.41	0.43	4.11	0.65	0.63
(2 locations)	.40	.42	3.91	.64	.60
Average deviation of individual results from mean chemical result					
	5.9	4.7	2.4	2.8	1.6
Average deviation from mean spectrographic result					
	1.7	4.1	2.2	2.8	1.3

copper in the sample, it is apparent that we can use a rule reading directly in percent copper, and this is generally done in routine work. Normally, in routine procedure the operator has only to align his rule with the aluminum peak, move the rule horizontally until an index mark intersects the curve, and then move it vertically to the copper peak and read percent copper. Thus, with a recording densitometer, the only numerical datum recorded for a particular determination is the final result. With a non-recording densitometer the procedure is essentially the same, except that numerical values for transmissions are read and recorded and the calculating board is equipped with a vertical logarithmic scale for plotting ordinates.

TABLE II. *Spectrographic and chemical analyses on duplicate samples.*

SAMPLE	% Cu SPEC.	% Cu CHEM.	% DIVERGENCE OF SPEC. AND CHEM. RESULTS
3924–27	4.11	4.01	2.5
3924–29	3.87	3.93	1.5
3924–31	4.06	3.97	2.3
3924–35	4.12	3.92	4.8
3924–41	4.05	4.01	1.0
3924–51	3.92	3.89	1.0
4018–5	3.97	3.92	1.3
4018–7	4.02	3.88	3.6
4018–11	4.12	3.88	6.2
4018–17	3.92	3.96	1.0
4018–19	4.01	3.92	2.3
4018–45	4.24	4.06	4.4
4018–51	4.16	4.14	.5
4018–55	3.95	3.98	.8
Average deviation of spectrographic and chemical analyses			2.40%

QUALITY OF RESULTS

The first requirement for a routine spectrographic method is, of course, that it will yield analyses accurately representing the composition of the sample tested. That we have met this requirement has been demonstrated in thousands of comparative spectrographic and chemical tests made both in our research laboratories and in our routine installations. Typical of the results obtained are those shown in Table I.

The spectrographic analyses were made by sparking ten locations in close proximity to each other on a machined surface from the interior of a cast aluminum ingot. A Gaertner L254 spectrograph and a Leeds and Northrup densitometer were used. The chemical analyses given were obtained on machinings from two carefully selected locations on either side of the region used for spectral analysis. It will be observed that, on a percentage basis, the largest divergences of spectrographic and chemical analyses were obtained in the case of silicon and iron. While this effect is typical of analyses on this particular alloy, it does not mean that the silicon and iron determinations are inherently less precise. It is simply the result of our standard practice of adjusting working conditions to give maximum precision for the larger constituents, consistent with satisfactory results for the other elements to be determined. The precision of any one of the determinations made can be increased appreciably by adjusting exposures and excitation conditions so as to favor that particular determination. In large scale tests made under conditions selected for the copper determination without regard for the determination of any other elements, we have reduced the average deviation of the copper results from the mean to less than two percent of the amount present. In our normal analytical procedures, however, the necessity for determining several elements simultaneously requires that our working conditions be a compromise among the best conditions for the various elements to be determined. Moreover, the precision of results obtained under these compromise conditions is, in general, equal or superior to that of the routine chemical methods which they have replaced and is quite adequate for all practical purposes.

Unfortunately, the mere ability to determine precisely the percent composition of the metal at the sparking surface is not sufficient. The analysis obtained must also be representative of the sample submitted and, further, of the mass of metal from which that sample is taken. The sampling problem, while encountered in any analytical method, is particularly difficult in spectrographic work and in the case of many materials which are otherwise well suited for spectrographic methods, spectrographic analysis cannot be made because the lack of homogeneity makes the sampling problem too difficult for routine work. In principle, at least, probably the best means of obtaining representative samples

are by the conversion of the material to a homogeneous liquid, or by thoroughly mixing a pulverized sample. Neither of these methods lends itself very well to the routine analysis of aluminum alloys. Not only are such methods excessively time consuming, but they also present excitation problems which we are not yet ready to meet. It is doubtful whether such samples can be excited with the reproducibility we now obtain with carefully prepared metallic electrodes. While we believe that such methods have their place in metallurgical work, particularly in the analysis of the so-called "rich alloys" or "hardeners," we have so far only employed them experimentally.

In most of our routine work the analytical samples are either circular or rectangular plates, cast in a cold mold. The specimens are about $\frac{1}{4}$ in. in thickness and freeze almost immediately in pouring. As with any type of casting, these samples are not entirely homogeneous and must, in turn, be sampled with some care. Comprehensive tests have been made to determine the distribution of various alloying elements in such samples, and we have found that when these samples are machined to a sufficient depth (usually $\frac{1}{32}$ in.) and sparked in the regions which freeze first, i.e., near the edges furthest from the inlet, the analyses obtained closely represent the sample as a whole.

In Table II are shown the results of a series of tests made in the course of our studies of sampling.

In these tests, the chemical and spectrographic analyses were made on separately cast specimens. The agreement of the spectrographic and chemical results is at least as good as we would expect to get had both sets of samples been analyzed chemically. These results were obtained on our Gaertner spectrograph and a Leeds and Northrup densitometer. Similar results are, of course, obtainable with the other types of equipment we are using.

While it is generally to be expected that the precision of spectrographic results turned out by a routine laboratory will increase with the experience of its personnel, we have been frequently surprised by the quality of the results turned out by our routine laboratories in the earliest stages of their development. As a matter of fact, the best agreement between spectrographic and chemical copper results we have yet obtained in routine operation is being turned out by a laboratory which has been in operation only about six weeks. In Table III are shown the first set of spectrographic results turned out by this laboratory and the subsequent chemical analyses which were made as a check on the accuracy of the calibrations. Since that time, frequent chemical checks on this laboratory work have shown that this unusually high precision is being maintained.

TABLE III.

SAMPLE	% COPPER SPEC.	% COPPER CHEM.	% DEVIATION
1103–1	4.61	4.67	1.3
1103–3	4.42	4.43	.2
1103–4	4.42	4.51	2.2
1103–7	4.48	4.69	4.5
1103–8	4.45	4.55	2.2
11098–2	4.21	4.26	1.2
11098–3	4.31	4.37	1.4
1107–1	4.61	4.71	2.1
1182–4	4.45	4.40	1.1
1183–9	4.45	4.40	1.1
Average deviation of spectrographic and chemical results			1.73%

In general, we are confident that any of our spectrographic laboratories can turn out copper analyses which will deviate from carefully made chemical analyses by a maximum of 5 percent and an average of less than 3 percent of the amount present. We have now reached a stage where suspicion is first directed at the chemical analysis when any serious disagreements are encountered, and we have found that an efficient spectrographic laboratory rarely loses an argument when composition is in dispute.

A Spectrographic Analysis of Iron for Tellurium*

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THE extensive development of alloys and the improvements in methods of testing and analyzing these metals are giving rise to an increasing realization of the importance of elements which are present in very small percentages. In some cases these small amounts are detrimental to the product and so, if present as impurities, they must be removed or kept below certain maximum limits of concentration. In other cases, small amounts of an element are being found to produce beneficial results, and if not present in the raw materials, can, with great advantage, be added to an alloy. An example of the latter case, described in British Patent No. 525,478 and soon to be described in a United States Patent, is the use of tellurium in iron. It has been found that the presence of several thousandths of one percent of tellurium in cast iron has the effect of keeping the carbon in the combined state during the pouring and solidification process but has little influence upon the subsequent annealing process. This makes it possible to use a relatively large amount of silicon to promote annealing and at the same time to be assured of obtaining white iron when the metal is poured. The result is that, for ordinary sections, the annealing time is greatly reduced and it is practical to cast much larger sections than when tellurium is not used.

This use of tellurium requires analyses covering the range of concentrations from 0.001 to 0.01 percent. In the development of new applications of the metal, frequent analyses must be made and in production it is desirable to check the composition of the metal from time to time. When scrap iron containing tellurium is used, the melt must be analyzed rapidly enough to permit the determination of the proper amount of tellurium to be added before the metal is poured. Although spectrographic methods are, in general, particularly suited to this type of problem, the analysis of tellurium presented some difficulties. This element had previously been considered one of the elements which did not respond to ordinary spectrographic methods. Only two papers on methods of analyzing for tellurium have been found in the literature. One[1] is concerned with the analysis for tellurium in bismuth and the other[2] is concerned with the analysis for tellurium in alloys of bismuth, lead and silver in both solutions and solid samples. In both cases the results of the analyses are of a semi-quantitative nature. No information on the analysis of iron for tellurium has been found and both of the articles cited describe methods different from the one which has been used in the present case.

Source of Light and Its Operation

The light source used is the high voltage alternating-current arc between metal electrodes. Preliminary experiments have shown that for this problem the alternating-current arc is superior to the direct-current arc and also to the condensed spark. This work, as well as that of other investigators[3] analyzing iron alloys for elements appearing in slightly higher percentages, shows that the direct-current arc has sufficient sensitivity but that the spectrum radiated cannot be well reproduced. The condensed spark can be controlled but does not afford the desired sensitivity.

The electrical circuit used for the arc is as follows: The primary of a 20 : 1 transformer is connected to a 118-volt power supply and the secondary is connected to the arc stand through a large ballast resistance which limits the arc current to 2.65 amperes. The resistance consists of a bank of specially wound heater coils, shown in Fig. 1. This resistor is well insulated, will carry up to 5 amperes, and is variable in 10 steps between 90 and 3890 ohms.

The samples are prepared in the form of $\frac{1}{4}$-inch cast rods. One end of each of two electrodes

* Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 21–23, 1941.

[1] H. Topelmann, Zeits. f. analyt. Chemie **82**, 284 (1930).
[2] Else Riedl, Zeits. f. anorg. Chemie **209**, 356 (1932).
[3] R. A. Sawyer and H. B. Vincent, J. App. Phys. **11**, 452 (1940).

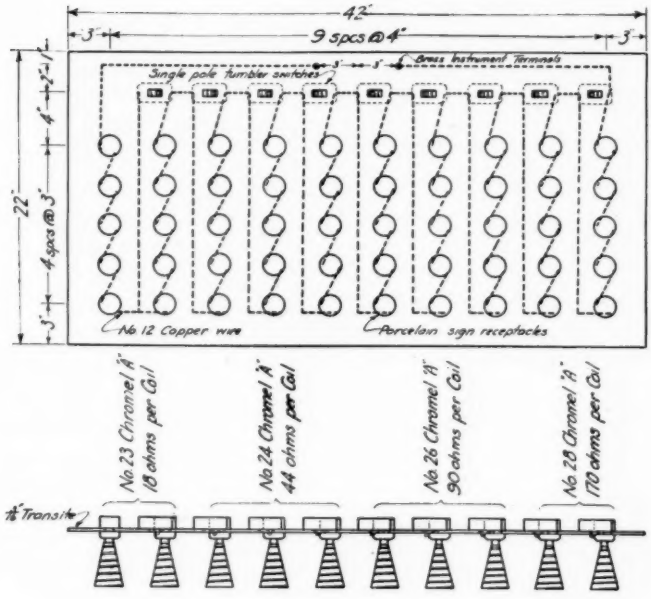
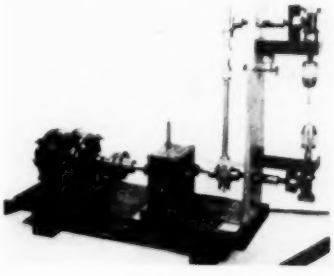
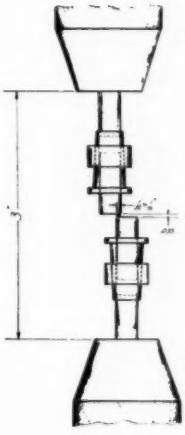
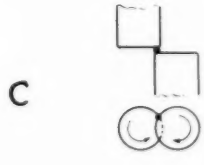

42"
3"
9 spcs @ 4"
3"
Single pole Tumbler switches
Brass Instrument Terminals
22"
4 spcs @ 3"
No 12 Copper wire
Porcelain sign receptacles
No 23 Chromel A" 18 ohms per Coil
No 24 Chromel A" 44 ohms per Coil
No 26 Chromel A" 90 ohms per Coil
No 28 Chromel A" 170 ohms per Coil
1/4" Transite

FIG. 1. Detail of special resistance bank.



A

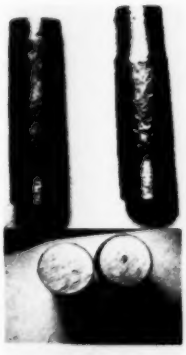




C

B

FIG. 2. (A) The electrode rotator. (B) The relative positions of the electrodes, also special chucks for holding short rods. (C) Direction of rotation.



Prepared Electrodes

Burned Electrodes

FIG. 3. A typical sample before and after arcing.

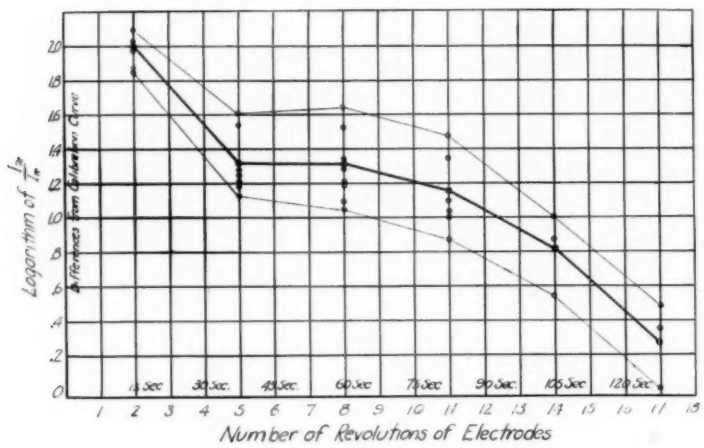


FIG. 4. Log ratios of line intensities for different preburning periods.

is ground flat and perpendicular to the axis on a surface grinder and the edges are made smooth on a metallurgical polishing table. The electrodes are mounted vertically in the electrode holder with their axes off-set with respect to each other, and are rotated during the exposure. Figure 2A shows the electrode rotator. The relative positions of the electrodes, and special chucks for handling short lengths, are shown in Fig. 2B. The arc is placed eight inches in front of the slit of the spectrograph and no condenser lens is used. The exposure is made during only the first revolution after the arc is started.

This method of arcing the sample produces a burned ring around the circumference of the end of each electrode as shown in Fig. 3. The purpose of rotating the electrodes is to increase sensitivity by melting a relatively large amount of sample and, at the same time, to have a method of arcing which can be well reproduced. Considerable care has been taken to determine the optimum values of arc current, gap length, speed of rotation and exposure time.

An arc current of 2.65 amperes was found to be satisfactory for covering the total range of concentrations of tellurium from 0.001 to 0.01 percent. Lower currents reduced sensitivity and therefore reduced the accuracy of determinations of the lower percentages; higher current arcs with electrode sizes and gap lengths used were unstable. The current has been reproduced in each exposure within plus or minus 0.05 ampere. A variation of 0.1 ampere introduces an error in the analysis of 4.0 percent.

The gap length used is 0.035 inch and the electrodes overlap approximately $\frac{1}{16}$ inch. This gap length is used because it gives the most satisfactory operation of the arc. If the electrodes are separated too far the arc will not be maintained; too small a gap may become bridged over with molten metal. There is a region of gap lengths between the approximate limits of 0.02 and 0.05 inch which can well be used with a potential of 2200 volts and a current of 2.6 amperes. However, after a gap length is selected it must be carefully reproduced for every exposure and the electrodes must be mounted in a way which will insure the maintenance of a constant gap during rotation.

The electrodes are rotated at the rate of 8 r.p.m. Since best results are obtained by making the exposure during only the first turn, both exposure time and reproducible arcing had to be considered in determining the optimum speed of rotation. However, since exposure time could be compensated for in other ways, the primary concern has been that of reproducing a uniformly burned area. If the electrodes are rotated too slowly, the arc burns on certain preferred spots instead of moving uniformly around the ring. This causes a variation in gap length and reduction of the total volume of metal burned. Turning the electrodes too rapidly also prevents the formation of a uniformly burned ring. It has

been found that the relative direction of rotation of the electrodes which gives the most stable operation of the arc is that shown in Fig. 2C. The overlapping sections of the surfaces move in the same direction and the arc is oriented so that the burning surfaces move toward the slit of the spectrograph.

The procedure of operating the arc for a short time before each exposure is not being used. However, such a preburning period was omitted only after a careful study of its effect upon sensitivity and reproducibility had been made. Figure 4 shows a series of measurements of line intensity ratios made from a single sample for each of six different preburning periods with rotating electrodes. For each determination the spectrum was exposed during two revolutions of the electrodes after a preburning time shown by the value of the abscissa. The heavy line is drawn through the averages and the light lines are the envelopes of the extreme values. These data show that the ratio of tellurium to iron line intensities decreases quite rapidly during about the first forty seconds and after that it decreases more slowly. In other words sensitivity is greatly reduced when the electrodes are preburned. Although the tellurium line could be measured in the spectrum of this particular sample after as much as two minutes of preburning, other data showed that this reduction in sensitivity could not be tolerated for samples which contained the usual concentration of tellurium. Better reproducibility might be expected if the electrodes were preburned about 40 seconds, because the ratio of line intensities remains more nearly constant for a time after that interval. However, the dispersion of the points in Fig. 4 indicates that better reproducibility was obtained with the shortest preburning time. When this study was carried still further, it was found that better reproducibility and much better sensitivity were obtained with no preburning. It was observed that, when the electrodes were rotated, their surfaces did not receive a uniform working or burning, but that a ring was burned around the edges and the area in the center of the end of each electrode was burned very little. When an exposure was made after any reasonable amount of preburning the arc would burn on unburned metal during a variable part of the exposure, thus giving poor reproducibility of the spectrum. If it were not necessary to rotate the electrodes to obtain the required sensitivity, it is quite possible that some preburning would be advantageous.

Analysis of the Spectrum

A specially designed double Cornu prism spectrograph has been used for the development of this method of analysis. However, some analyses have been made with equal success on a Bausch and Lomb large Littrow spectrograph. In this analysis procedure the 2385.76A line of tellurium must be resolved from the iron lines 2385.58 and 2385.95A.

The spectrum is recorded photographically and the analysis is made by the internal standard method. The analysis line is the 2385.76A line of tellurium. Iron, in which tellurium has so far been used, has not contained such elements as chromium, vanadium, and cobalt which have lines that would interfere with this analysis line.

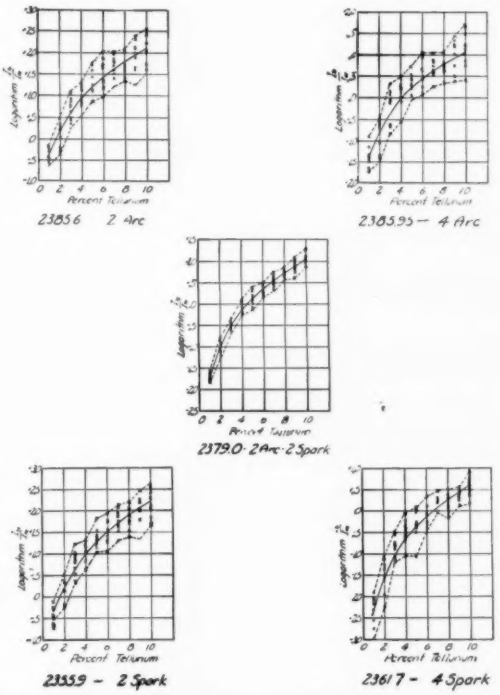


FIG. 5. Data showing the reproducibility of the log ratio of line intensities for different internal standard lines.

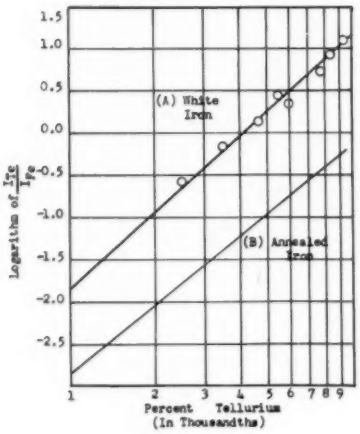


FIG. 6. Analytical curves.

The 2378.98A iron line has been used as the internal standard. This selection was made as a result of a careful study of several different iron lines having various excitation characteristics. Some lines tried are distinctly spark lines, others are arc lines and still others have approximately equal intensities in the arc and spark. Figure 5 shows representative data on five different iron lines. Using each as an internal standard the log ratios of line intensities were measured for the ten standard samples. These values were plotted as shown; the dotted lines indicate the envelope of the extreme values. It was found that of those lines studied the 2378.98A line, recorded in the *M.I.T. Wavelength Tables* as having an intensity of 2, in both the arc and the spark, gave the most reproducible results. The analysis line is listed with an intensity of 600 in the arc and 300 in the discharge tube.

The photographic plates are calibrated by means of a rotating logarithmic sector disk having five steps with an aperture ratio 2 : 1. An iron arc placed four feet from the slit of the spectrograph is used as the calibrating source. Both direct-current arcs and alternating-current arcs have been used for this purpose. However, if the latter is used the rotating disk must be run at such a speed that synchronization does not take place between the arc and the disk openings.

The process of establishing an analytical curve has required some special consideration because of the difficulty in determining the concentration of tellurium in standard samples. Samples which have been used as standards and as test specimens in developing the method were prepared by adding known amounts of tellurium to melts of iron. However, it was not possible to calculate the percent of tellurium from the amount added because (1) unknown amounts of tellurium are lost from the molten metal by evaporation (tellurium boils at 1390°C and iron melts at 1535°C) and (2) due to the conditions under which the samples were prepared there was some uncertainty as to the amount of iron used. The analysis for these small percentages of tellurium by chemical wet methods is tedious and the agreement between different determinations is not good; the time and amount of material required make it impractical to carry out large numbers of analyses from which to obtain good averages. Table I shows the data on the standard samples. Figure 6A shows the best available chemical analyses plotted against the log ratio of spectrum line intensities and an analytical curve which has been drawn to fit these points. The accepted analyses of the standards shown in column 4 of Table I were arrived at by assuming the log ratios to be correct, since they are averages of large numbers of observations, and reading percentages from the accepted analytical curve.

Chemical determinations were not available for samples containing less than 0.0025 percent. In order to make spectrographic analyses in this region, the analytical curve has been extrapolated to include the lower values. In making this extrapolation it is assumed that enough points have been used to establish the curve in the upper region and that the ratio of

TABLE I.

Sample No.	Percent Tellurium Added	Chemical Analysis	Corrected Analysis
3	0.001	—	0.0012
6	.002	—	.0022
9	.003	0.0025	.0028
2	.004	.0035	.0038
8	.006	.0047	.0047
5	.007	.0060	.0055
1	.005	.0055	.0060
4	.008	.0078	.0073
7	.009	.0082	.0086
10	.010	.0993	.0097

the line intensities is proportional to the concentration.

It might be pointed out that the analytical curve could be used to express not only the relation between ratios of line intensities and chemical analyses but also, in the absence of chemical values, the ratio of line intensities to physical or metallurgical properties such as annealing time. If the latter properties should be proportional to the concentration of tellurium the second proposed analytical curve would be similar to the curve based on chemical analyses. Some of the present work was done with the latter possibility in mind and it was only after sufficient chemical values became available that the conventional analytical curve was used.

The Effect of Annealing

The analytical curve shown in Fig. 6A is for the analysis of white iron, that is, iron in which the carbon is completely in combined form. The present procedure has been particularly developed for the control analysis of iron at pouring. That this metal will be in the white iron state is assured by the presence of the tellurium itself, which is added as an inhibitor of graphitization during solidification.

It has been found that as the sample is annealed, or in other words as the carbon is precipitated, the relative intensities of the tellurium and iron spectra change. Figure 6B shows an analytical curve for annealed iron. Since the samples used to obtain this curve are some of the same rods used to obtain the white iron curve, except that they have been put through an annealing process, an estimation of the change in relative intensities of tellurium to iron in passing from a state of dissolved carbon to free carbon can be obtained. As shown by the two analytical curves, the ratio of the intensity of the tellurium line to that of the internal standard iron line decreases when the iron is annealed. This would indicate a decrease in the amount of tellurium present. However, chemical analyses of samples containing 0.005 percent or more have shown that the tellurium is not lost in the annealing process. Furthermore, it has been found that the magnitude of this divergence of relative intensities depends upon the extent to which the carbon is precipitated, reaching a maximum departure or minimum value of relative intensities when the carbon is completely freed.

In practice, when iron which contains some free carbon is to be analyzed, precautions must be taken to use the correct analytical curve. This will apply to most samples cut from fabricated parts. The condition of the carbon in the iron can be determined by a metallographic study. If part of the carbon is found to be combined it can be precipitated by putting the sample through an annealing process. By this method all pieces not in the white iron state can be brought to the same end condition and a single analytical curve for annealed iron can be used.

Table II.

Percent	Number of Samples Analyzed	Max. Error %	Aver. Error %
0.0012	10	16.0	4.1
.0022	7	8.4	4.2
.0028	11	14.2	3.8
.0038	10	10.2	3.7
.0047	14	14.8	7.0
.0055	11	7.2	2.8
.0060	23	6.7	3.7
.0073	10	6.9	3.7
.0086	7	4.7	2.6
.0097	9	6.2	2.9
Summary	112	16.0	4.0

The fact that the relative intensities of the spectra of tellurium and iron are changed when a sample is annealed puts a limitation on the repeated arcing of standards. It was found, when a single set of rods was re-used several times, that even when the burned metal was carefully removed there was an apparent diminution of the amount of tellurium present. Observations of the spark thrown off during regrinding of the surfaces indicated that a change of state had been brought about by the arcing process. Metallographic studies showed that this was due to a gradual precipitation of carbon with each heating and cooling involved in making an exposure. It becomes necessary, therefore, to use a new piece of metal for the electrodes each time a reference to the standard is made, and in grinding the surface care should be taken to prevent overheating.

No effects produced by extraneous elements

TABLE III.

DATE	PERCENT Te	PERCENT DEV.	(DEV. %)²
8-22-40	0.0060	0.66	0.44
	.0061	0.99	0.98
	.0059	2.32	5.38
	.0062	2.65	7.02
8-23-40	.0061	0.99	0.98
	.0062	2.65	7.02
	.0057	5.63	31.70
	.0062	2.65	7.02
9-4-40	.0063	4.30	18.49
	.0060	0.66	0.44
	.0056	7.28	53.00
	.0059	2.32	5.38
9-5-40	.0061	0.99	0.98
	.0061	0.99	0.98
	.0064	5.96	35.52
9-5-40	.0057	5.63	31.70
	.0062	2.65	7.02
	.0064	5.96	35.52
	.0059	2.32	5.38
9-11-40	.0058	3.97	15.76
	.0061	0.99	0.98
	.0064	5.96	35.52
	.0057	5.63	31.70
Average 0.00604			$\Sigma d^2 = 338.91$

Standard Dev. $= (\Sigma d^2/n-1)^{\frac{1}{2}} = 3.93\%$

have been observed. The compositions of the samples to which tellurium has so far been added have varied very little except for the concentrations of tellurium and silicon. Amounts of silicon ranging from 1.2 to 1.8 percent have been used and there has been no evidence that this variation affects the analysis for tellurium.

SPEED, ACCURACY, AND REPRODUCIBILITY

The time required for one operator to prepare a sample and complete its analysis is, at the present time, about thirty minutes. With high speed processing of the plates and with the use of a tool especially designed for preparing the ends of the electrodes, it should be possible to reduce this time to about 15 minutes.

It has not been possible in this work to determine the accuracy of spectrographic analyses by comparing them with chemical analyses. There has been poor agreement between chemical analyses of the same sample and, as mentioned above, it has not been considered practical to make a large number of chemical analyses of each sample. On the other hand, the reproducibility of the spectrographic analyses has been demonstrated by comparing repeated analyses on each of a number of samples. Table II shows the results of a representative set of 112 measurements made on the standard samples. Column 1 gives the percent tellurium as established by the analytical curve (this is the value given in column 4, Table I) columns 3 and 4 give deviations from the value in the first column. These measurements have not all been made on the same plate nor have they been made on the same day. Table III shows the day-to-day reproducibility of the analyses of one of the samples. An analysis of the 112 measurements summarized in Table II shows that the standard deviation is 5.14 percent. Assuming a normal distribution of errors it is, therefore, to be expected that in only 31.7 percent of the cases will the error be greater than 5.14 percent and only once in 375 times will the error be greater than three times this amount.

It has been shown that a spectrographic method can be used to analyze iron for tellurium and it appears that this is the only method which provides the speed and accuracy required in a production analysis. The range of concentrations covered at present is 0.001 to 0.01 percent. Analyses can be reproduced within 5 percent; in the case of a sample containing about 0.005 percent the analysis is made within 0.0003 percent of the total sample.

Spectrochemical Determination of Lead, Cadmium, and Zinc in Dusts, Fumes, and Ores[1]

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INTRODUCTION

A SPECTROCHEMICAL method is described for the determination of lead, cadmium, and zinc in samples of dusts and fumes collected with the Barnes electrostatic precipitator.[5] The method also may be applied to other samples containing lead, cadmium, and zinc. The technique of the method involves the use of solutions containing an internal standard[6] and a spectroscopic buffer.[7,8] A drop of solution is evaporated on the plane end of each of a pair of electrodes. Copper is employed as the electrode material to eliminate the effect of electrode absorption. The spectra are photographed through a step sector[9,10] and measured with a nonrecording photoelectric densitometer.

APPARATUS

A large Littrow-type prism spectrograph with quartz optics, giving a 700-mm spectrum between 2100A and 8000A, was used. The spectra were excited with a 2200-volt alternating-current arc[11] supplied by a 15-kva dry-type transformer with a four-coil secondary which permitted the use of 1100, 2200, or 4400 volts across the arc at the full capacity of the transformer. A number of cone-type heater resistances arranged in a series-parallel bank with switches to change the resistance of the system were used in the secondary circuit of the transformer to limit the current through the arc.

The arc stand is completely enclosed in a wooden hood to protect the operator from electric shock. The hood is connected to the exhaust system of the building to carry off fumes generated in the arc and is provided with two windows for observation and with a source-aligning system which permits the operator to observe a magnified image of the arc during an exposure. The source-aligning system employs an achromatic lens of small aperture mounted in a fiber tube which slides in a mounting fixed on the wall of the hood. Light from the arc is gathered by the lens, reflected by a mirror held in an adjustable mounting on a wall behind the hood, and focused on a scale fixed on the hood at the eye level of the observer.

As the hood is provided with a door switch, which prevents turning on the power until the door is closed, and as it was desired to have the controls grouped conveniently, knobs for moving each electrode vertically and for moving the arc laterally are brought to the outside of the hood by means of flexible-cable connectors which are insulated from the arc stand by hard-rubber sections in the shafts. Small adjustments in the arc current may be made during an exposure by means of a slide-wire rheostat mounted in the hood in series with the arc and controlled from the outside by an insulating rope in front of the hood. Thus, all controls for preparing a spectrogram are grouped at one end of the spectrograph so that the operator may use the instrument with a minimum of lost motion.

Figure 1 shows a lamp mounted on a pivot inside the hood so that it may be used with the

[1] Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 21–23, 1941. Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

[2] Junior physicist, Gas and Dust Section, Bureau of Mines Experiment Station, Pittsburgh, Pennsylvania.

[3] Assistant physicist, Gas and Dust Section, Bureau of Mines Experiment Station, Pittsburgh, Pennsylvania.

[4] Chief chemist, Health Division, Bureau of Mines.

[5] E. C. Barnes and G. W. Penney, "An electrostatic dust weight sampler," J. Ind. Hyg. and Tox. **20**, 259–265 (1938).

[6] W. Gerlach and E. Schweitzer, *Foundations and Methods of Chemical Analysis by the Emission Spectrum* (A. Hilger, Ltd., London, 1931).

[7] G. O. Langstroth and D. R. McRae, "Transport of materials in sources for spectroscopic analysis," Can. J. Research **16A**, 61–74 (1938).

[8] T. M. Hess, J. S. Owens, and L. G. Reinhardt, "Analysis of organic materials for traces of metallic impurities," Ind. and Eng. Chem., Anal. Ed. **11**, 646–649 (1939).

[9] B. F. Scribner, "The comparison of line intensities in spectrochemical analysis," *Proceedings of the Fifth Summer Conference on Spectroscopy* (John Wiley, New York, 1938), pp. 61–74.

[10] L. W. Strock, *Spectrum Analysis with the Carbon Arc Cathode Layer* (A. Hilger, Ltd., London, 1936).

[11] O. S. Duffendack and K. B. Thompson, "Developments in the quantitative analysis of solutions by spectrographic means," Proc. A. S. T. M. **36**, 301–309 (1936), Part 2.

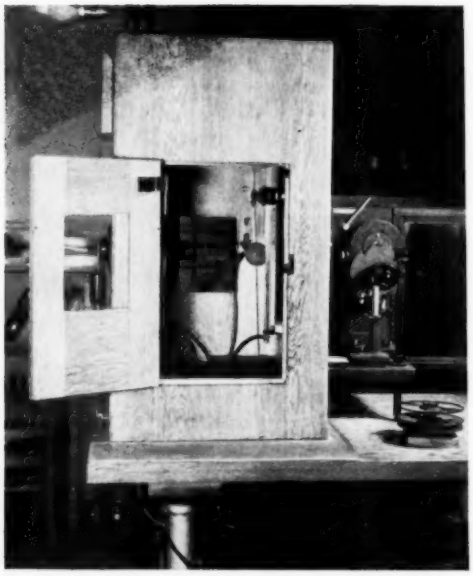

FIG. 1. Interior of the hood enclosing arc and spark stand.

source-aligning system to fix the position of the electrodes before the arc is struck. The electrode separation may be set within 0.03 mm with the aid of graduations in the scale on the hood.

Figure 2 is a photograph of the non-recording photoelectric densitometer used to measure the spectrograms. Figure 3 is a sketch of the optical diagram of the instrument. The plate holder is mounted so that any part of a plate 4 inches by 10 inches or smaller may be moved by hand into the path of the light beam. A spectrum line is moved across the slit in front of the photo-cell by means of a millimeter pitch screw threaded into a nut on the plate holder. The screw may be turned by hand for measuring line separations or by a small reversible motor through a worm and gear for measuring line densities. The indicating system consists of a barrier-layer photo-cell connected with a sensitive short-period galvanometer. A potentiometer circuit, which does not affect the response of the photo-cell or the galvanometer,[12] is used to adjust the zero point, and rheostats in the lamp circuit are used to control sensitivity.

[12] A description of this circuit will be presented in another paper.

DEVELOPMENT OF METHOD

In a preliminary study, graphite electrodes were employed to hold the sample in the arc. These electrodes were treated with kerosene to prevent absorption of the sample by the graphite. It was found that the results obtained with these electrodes varied erratically. To determine the cause of the erratic results spectra were photographed using a short slit and moving the plate down the length of the slit at 15-second intervals. This procedure made it possible to study the variation in intensity ratio between a line due to an unknown and a line due to the internal standard during an exposure. Figure 4 gives a series of curves correlating intensity with time. Curves *A* show the results for kerosene-treated electrodes. In interpreting these curves it was assumed that the first sharp drop in intensity with time was due to volatilization of the salts that had crystallized on the surface of the electrodes. The remainder of each curve was thought to be due to heating of the electrodes and volatilization of the material that had been absorbed. To test these hypotheses, spectra were prepared, as described above, for the same sample on untreated graphite electrodes (Fig. 4, B) and on copper electrodes (Fig. 4, C). As the minimum did not occur when untreated graphite electrodes or copper electrodes were used, the hypotheses seemed justified.

Computation of the intensity ratio with the three sets of electrodes, made by taking the ratio of the areas under the curves, showed a definite correlation between the extent of the absorption

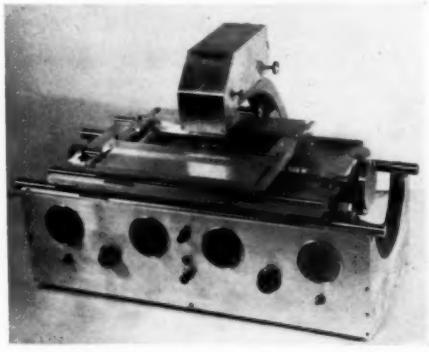

FIG. 2. A non-recording densitometer used for making density measurements,

and the intensity ratio. It was found that the smaller the absorption, the greater was the intensity ratio for a given sample. Further tests of this type on kerosene-treated electrodes showed that there was considerable variation in the porosity of the graphite electrodes which accounted for the erratic results obtained with graphite.

The evidence of the effect of absorption of the samples by the electrodes on the intensity ratio led to studies to find a coating for the graphite electrodes which would be more effective than kerosene in preventing absorption of the samples. Collodion, wax, and other materials were tried, but no entirely suitable coating was found. The improvement in the precision of the results with the copper electrodes led to their adoption. Tests made at various times indicated that there was not enough lead, cadmium, or zinc in the commercial copper used to affect the results of analyses obtained by this method. It was found, however, that the concentration of acid in the samples had to be maintained within reasonably close limits, as the results were affected by gross changes in the quantity of copper nitrate formed on the electrodes. No difficulty was experienced with spattering of the sample from the electrodes. It was also necessary to keep the concentration of negative radicals other than the nitrate ion to a minimum to prevent the formation of compounds other than copper nitrate on the electrodes. For example, when iodine was added to samples in the chemical analysis for lead by the chromate method, copper iodide formed on the electrodes and changed the condition of the arc during exposure. This phenomenon caused considerable difference between the chemical and spectrographic results. Removal of the iodine from the samples by heating and re-analysis gave results which agreed with those obtained chemically.

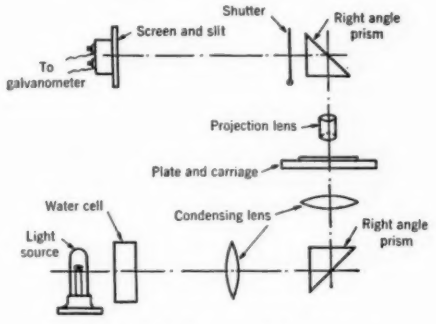

FIG. 3. Optical diagram of densitometer

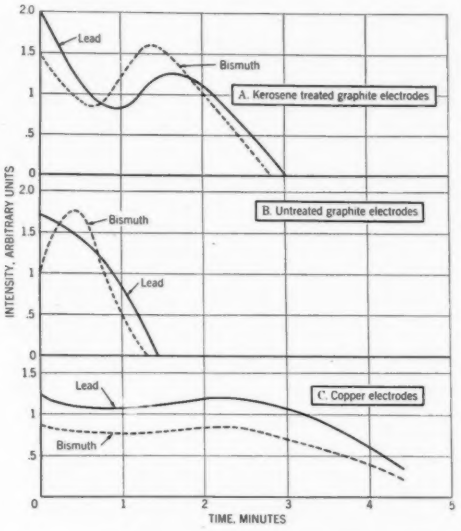

FIG. 4. Curves showing variation of intensity with time for a lead and a bismuth line.

Changes in the electrode separation affected the intensity ratios. This result was in accord with the work of Duffendack.[13] Figure 5 shows the relationship between intensity ratio and electrode separation. These curves were used in choosing the most desirable separation. Although greater sensitivity could be obtained for zinc by using an electrode separation smaller than 1 millimeter (the value chosen), the loss in precision caused by the rapid change in the zinc intensity ratio with a smaller separation was more detrimental than the lower sensitivity with the larger separation.

The effect of changes in the arc current was also investigated. The results were not greatly affected by variations in the current; however, the use of a large-capacity supply line eliminated large-scale variations in the arc current, and the variable resistance in series with the arc made

[13] O. S. Duffendack and R. A. Wolfe, "Analysis of caustic liquors for traces of impurities," Ind. and Eng. Chem., Anal. Ed. **10**, 161–164 (1938).

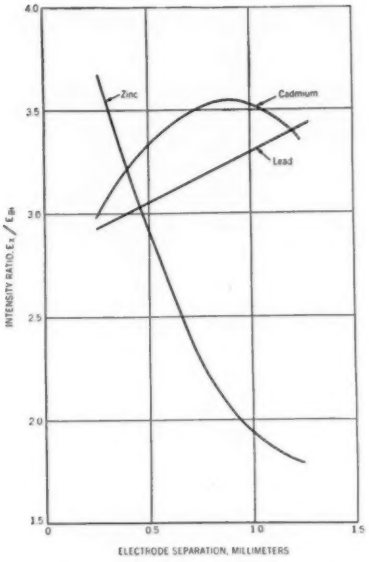

FIG. 5. Variation of intensity ratio with electrode separation.

it possible to control the current within 0.05 ampere.

ANALYTICAL PROCEDURE

Preparation of samples

The air-borne dusts and fumes were collected on aluminum foil with a Barnes electrostatic precipitator. Qualitative analysis of the aluminum foil showed that it contained appreciable quantities of iron, magnesium, manganese, copper, and silicon, but no lead, cadmium, or zinc was detected.

The samples were weighed and then washed from the foils into 250-ml beakers, using a rubber policeman, distilled water, and about 50 ml of a 1-normal solution of C.P. nitric acid to insure complete removal of the sample from the foil. Experimental tests showed that the amount of foil taken into solution by this treatment did not affect the results. The beakers were placed on a hot plate and the solutions evaporated just to dryness. The residues were taken up in 8 ml of 1-normal nitric acid and transferred to 50-ml volumetric flasks. One ml of a solution containing 25 mg per ml of bismuth in 1-normal nitric acid was added to each sample as an internal standard, and 2 ml of a solution containing 250 mg per ml of sodium nitrate in distilled water was added to each sample as a spectroscopic buffer. The quantity of solution was then made up to 50 ml by adding distilled water. The nitric acid content, about 0.2 normal, was sufficient to prevent precipitation of the bismuth from the solutions.

For gross samples, such as ores or pieces of metal, a weighed portion of the material was dissolved in 5-normal nitric acid, evaporated to dryness, and treated in the same manner as the air-borne samples.

Preparation of electrodes

The arc electrodes were prepared from commercial-grade copper rod 0.635 cm (0.25 in.) in diameter, cut into 1.60-cm (0.625-in.) lengths. Each piece was faced off on a lathe, the outer surface cleaned with a file, and the edge at the faced-off end slightly beveled with a file. The electrodes were inserted in a rack, and one drop of solution was placed on each electrode with a medicine dropper. The racks were placed in an oven, and the temperature was raised to about 120°C. The solution evaporated in about 30 minutes, leaving the ends of the electrodes covered with the dried salts.

Preparation of spectrograms

The prepared electrodes were placed in the arc stand, and the separation between them was fixed carefully at 1 millimeter by observation of the image of the electrodes projected on the viewing scale. The spectrograph shutter was opened, the arc turned on, and a 3-minute exposure taken through a 0.050-mm slit with a step sector rotating in front of the slit at about 2,250 r. p. m. Three minutes was chosen as the least exposure that would give the required sensitivity. Longer exposures increased the sensitivity without materially affecting the reproducibility of the results. The arc current

TABLE I. *Line pairs used for analysis.*

	Spectral Lines in Angstroms	
Element	Element	Internal Standard (Bismuth)
Lead	2,833.1	2,938.3
Cadmium	3,261.1	3,397.2
Zinc	3,345.0	3,397.2

was maintained carefully at 3 amperes and the electrode separation at 1 mm throughout the exposure. After exposure, the plates were processed in a thermostatically controlled, constant-temperature tank maintained at 65°F. Eastman Type 103–0 plates were used with Eastman D-19 developer to obtain high sensitivity. After the plates had been processed and before measurement, they were dried in a blast of warm air.

Plate measurement

Table I shows the line pairs used in the analyses. Bismuth was used as the internal standard for the three elements to be determined. In each spectrum, four steps, lying between densities of 0.02 and 0.50, were measured for each of the two bismuth lines, and two steps (one step if the line was very faint) were measured within the same density range for each element to be determined. The galvanometer deflections for the bismuth lines were plotted against the relative intensities given by the sector openings for the steps measured. The intensity of the lead, cadmium, and zinc lines was determined from these curves. The ratio of the intensity of the unknown line to that of the internal standard line was used to determine the concentration of the unknown in the sample. This method of measurement, with a step sector, made possible the use of a single-line pair over a wide range of concentrations without measuring high densities. The restriction to densities less than 0.50 tended to diminish the Schwarzschild-Villiger effect[14] in the densitometer.

In the analysis of samples containing small quantities of cadmium and zinc, where the cadmium and zinc lines could be measured only in the first few steps of the spectrogram, it was necessary to correct for the background. This correction was made by measuring the galvanometer deflection due to the background immediately adjacent to a line, converting this measurement to the intensity of the background by means of the calibration curve obtained from measurements on the internal standard line, and subtracting the background intensity from the computed intensity of the line before determining the intensity ratio. A correction of this type gave reproducible results for background densities up to 0.10, which agrees with the results of Strock.[10]

PREPARATION OF WORKING CURVES

Figure 6 shows the working curves prepared from measurements made on standard solutions containing the test elements in the range between 0.001 mg per ml and 0.50 mg per ml, the buffer, and the internal standard. The curves indicated the range over which the method might be applied. Further tests were made to determine whether the ranges might be extended in either direction. For lead, it was found that the results were valid between 0.0004 mg per ml and about 0.10 mg per ml (0.02 to 5.0 mg in 50 ml of solution). The upper limit was determined as the region where the slope of the working curve became so low that accurate determinations of the concentration could not be made. The part of the curve for lead above a concentration of 0.10 mg per ml may be used for an approximate value, or the sample may be diluted for more accurate measurements. For cadmium the useful portion of the working curve extended from 0.0005 mg per ml to about 0.30 mg per ml (0.025 to 15 mg in 50 ml). The lower limit was fixed by the background due to halation from the dense 3,247.6A and 3,274.0A copper lines which lie on either side of the 3,261.1A cadmium line. For zinc the useful portion of the working curve extended from 0.005 mg per ml to 1.0 mg per ml (0.25 to

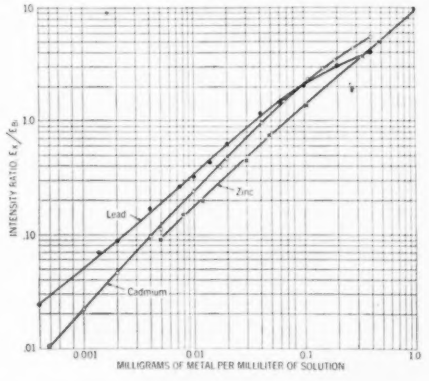

FIG. 6. Curves showing relation between relative intensity and metal concentration.

[14] W. E. Forsythe, *The Measurement of Radiant Energy* (McGraw-Hill, New York, 1937), p. 285.

TABLE II. *Spectrographic analysis of synthetic samples containing lead, cadmium, and zinc.*

Sample No.	Lead Milligrams Added	Lead Milligrams Found	Percent Error	Sample No.	Cadmium Milligrams Added	Cadmium Milligrams Found	Percent Error	Sample No.	Zinc Milligrams Added	Zinc Milligrams Found	Percent Error
5	0.070	0.074	+6	7	0.11	0.10	−9	1	0.22	0.21	−5
14	.37	.36	−3	1	.25	.25	0	9	.49	.35	−29
3	.67	.62	−7	13	.35	.33	−6	12	.73	.77	+5
9	.96	.94	−2	11	.85	.85	0	5	1.10	1.13	+3
2	2.30	2.37	+3	14	2.10	2.15	+2	15	1.80	1.85	+3
6	3.75	3.63	−3	5	3.30	3.43	+4	6	2.40	2.40	0
11	4.80	4.83	+1	15	4.90	4.80	−2	3	4.10	4.30	+5
15	5.20	5.33	+2	12	5.50	5.60	+2	13	5.90	6.27	+6
13	6.70	7.33	+9	9	5.90	5.63	−4	8	6.80	6.30	−7
4	7.60	7.00	−8	3	6.20	5.93	−4	2	8.40	8.33	−1
7	9.10	7.50	−18	4	7.60	7.33	−3	10	9.30	8.87	−5
1	9.70	10.6	+9	8	9.40	9.05	−4	14	10.2	10.2	0
8	12.5	11.4	−9	2	12.7	13.8	+9	7	12.5	11.3	−10
12	13.1	14.9	+14	10	14.0	13.7	−2	4	13.3	13.3	0
10	14.7	11.7	−20	6	14.8	15.7	+6	11	14.0	15.5	+11

TABLE III. *Comparison of chemical, dropping mercury electrode, and spectrographic analyses of air-borne dust samples containing lead.*

Sample No.	Chemical	Lead, mg D. M. E.*	Spectrograph	D. M. E.*/Chem.	Spec./Chem.	Spec./D. M. E.*
3068	2.75	2.85	2.85	1.04	1.04	1.00
3072	4.77	4.71	4.70	.99	.99	1.00
3083	6.38	6.14	5.75	.96	.90	.94
3087	10.2	10.7	10.8	1.05	1.06	1.01
3091	6.60	6.65	6.70	1.01	1.02	1.01
3086	—	.48	.43	—	—	.90
3090	—	.26	.26	—	—	1.00

TABLE IV. *Comparison of chemical, dropping mercury electrode, and spectrographic analysis of zinc ore and spelter.*

Sample No.	Percent Lead Chemical	Percent Lead D. M. E.*	Percent Lead Spectrograph	Percent Cadmium Chemical	Percent Cadmium D. M. E.*	Percent Cadmium Spectrograph	Percent Zinc Chemical	Percent Zinc D. M. E.*	Percent Zinc Spectrograph
1	1.58	1.53	1.4	0.24	0.31	0.22	57	56	59
2	.15	.14	.13	.13	.15	.13	56	53	53
3	.15	.13	.12	.12	.14	.14	53	51	54
4	.60	.59	.58	.19	.19	.17	61	60	64
5	.16	.14	.15	.13	.14	.13	63	60	63
6	.12	.12	.13	.04	.037	.034	65	64	65
7	.26	.29	.30	.078	.13	.11	99+	100	100
8	.42	.43	.47	.027	.024	.028	99+	100	93

* Dropping mercury electrode.

50 mg in 50 ml). The lower limit for zinc was fixed by the background radiation due to bands in the vicinity of the 3,345.0A zinc line.

RESULTS OF ANALYSES

To test the validity of the technique and the analytical curves, 15 synthetic samples made outside the laboratory were analyzed. The samples were made up in 50-ml volumetric flasks, and their composition was unknown to the analyst. Table II gives the results of these analyses, listed in order of increasing quantities of the unknowns. Each analysis in the series is the average of five exposures. For the eight samples containing less than about 5 mg of lead, i.e., for samples within the range of the curve for lead, the maximum error was 7 percent of the amount present and the average error 3.4 percent. For the 15 samples containing cadmium within the range of the curve for cadmium, the maximum error was 9 percent of the amount present and the average error 3.6 percent. For the 15 samples within the range of the curve for zinc, the average error was 6.1 percent of the

amount present. If the result for sample 9 is disregarded, the maximum error for the 14 remaining samples would be 11 percent of the amount of zinc present and the average error 4.5 percent.

Practical application has been made of the method in the analysis of air-borne dusts and fumes and zinc ores and spelters.

Table III presents analyses of seven samples of dust containing lead within the range of the method. Five of the samples were analyzed chemically by the chromate method, and all seven were analyzed using the dropping mercury electrode.[15] The maximum difference between the chemical and spectrographic results was 10 percent of the amount present, and the average difference for the five samples was 5.6 percent. The maximum difference between the dropping mercury electrode and the spectrographic results was 10 percent of the amount present, and the average difference for the seven samples was 2.6 percent. The spectrographic analyses reported in this series are averages of three exposures.

Table IV gives the results of analyses of eight gross samples of zinc ore, sintered zinc ore, and zinc spelter.[16]

Two hundred milligrams of each sample was dissolved in nitric acid. One-fourth of the solution was used for the spectrographic analyses and the remainder for analysis with the dropping mercury electrode. The agreement among the three methods was good, the deviations being of the same order as those previously cited.

[15] The chemical analyses reported in this table and all analyses with the dropping mercury electrode were made by Florence L. Feicht, junior physicist, Health Division, Bureau of Mines.

[16] The samples were supplied by the American Zinc & Chemical Co., Langeloth, Pennsylvania. The results of the chemical analyses were obtained in the course of regular control analyses performed under the direction of J. O. Butler, chief chemist of this company. Lead was determined by the molybdate method, zinc by the ferricyanide method, and cadmium by precipitation as the sulfide, solution, reprecipitation by aluminum, and titration with ferricyanide.

An Infra-Red Spectrometer for Industrial Use*

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INTRODUCTION

THE possibility of using infra-red spectroscopy for analytical purposes was recognized as long ago as 1881 when Abney and Festing[1] discovered that all hydrocarbons absorb infra-red radiation at a wave-length of about 3.4 mu. Between 1905 and 1908 Coblentz[2] examined the absorption spectra of an extended series of compounds, including about 20 hydrocarbons, and discovered several other bands characteristic of functional groups such as C=O, OH, SH, etc., but experimental difficulties prevented application of the spectra to practical problems.

From 1908 to 1928, infra-red investigations of polyatomic molecules were largely confined to attempts to discover absorption bands characteristic of functional groups. With the discovery and interpretation of the Raman effect (1928), the importance of these spectra was brought to the attention of a wider audience and the interest of investigators turned to attempts to determine from spectral data the physical properties of molecules, such as the entropy, the free energy, the heat capacity, etc. These attempts have been very successful in the case of simple compounds (ethane, methane, ethylene, etc.) and it seems likely that the method will work for much larger molecules.

Only within the past decade have efforts been made to apply infra-red and Raman spectra to the routine identification of chemical compounds. Until recently this work has not been very fruitful in petroleum analysis because the pure

* Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 21–23, 1941.

[1] W. de W. Abney and E. R. Festing, Phil. Trans. **172A**, 887 (1881).

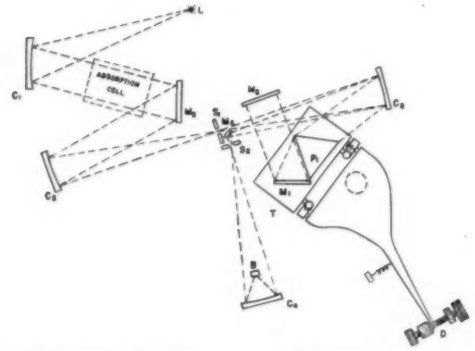
[2] W. W. Coblentz, Carnegie Institute, Washington, Publication **35**, and following volumes.

components have not been available and only academic laboratories have been equipped for infra-red research. In the instances where investigations have been carefully and intelligently performed, the usefulness of infra-red spectroscopy has been immediately apparent.

Wright, in a recent paper,[3] has pointed out several different fields of industrial research or control where infra-red studies would be of value. The present paper describes a new spectrometer that has been designed for industrial use where speed, convenience and ruggedness as well as accuracy are of great importance. Some applications of the instrument to the analysis of petroleum fractions are also presented.

Definitions

The term infra-red applies to radiations lying in the wave-length range 0.7 mu (7000A) to 500 mu. Because of experimental considerations only rays of wave-length shorter than 25 mu are at present useful for analytical purposes. This section of the infra-red spectrum is usually referred to as the near infra-red. Absorption bands found in this region are associated with changes in the vibrational and rotational energies of the absorbing particles and are known as "vibrational bands" (or vibration-rotation bands). It may be shown that the frequency of a particular type of vibration is determined by the spatial configuration of the vibrating particles, the masses of the particles and the forces acting between the particles. For example, the isomeric molecules, *n*-butane and isobutane, which differ in shape, produce different vibrational spectra.



L—light source (Globar)
M_1, M_2, M_3, M_4—plane mirrors
C_1, C_2, C_3—parabolized mirrors $f/5$
C_4—elliptical mirror
S_1, S_2—slits
P—prism
B—thermocouple
D—driving mechanism

FIG. 1. Infra-red spectrograph light path.

FIG. 2.

Apparatus

The spectrometer is similar in many respects to that designed by Gershinowitz and Wilson.[4] The optical path is shown in Fig. 1. The familiar Wadsworth-Littrow mounting is employed.

The radiation from "*L*" is collimated by C_1. Absorption cells are placed between C_1 and M_3. After reflection from M_3 the radiation is focused by C_2 on slit S_1 and is then collimated by the mirror C_3. Parallel light passes through the prism *P* at minimum deviation and is reflected from the Wadsworth mirror M_1 to the Littrow mirror M_2. It then returns through the prism at an angle slightly different from minimum deviation so that after being reflected from C_3 and M_4 it is focused on the second slit, which is one of the foci of the ellipsoidal mirror C_4. After passing through the second slit the radiation is reflected from the mirror C_4 which has a

[3] Norman Wright, Ind. Eng. Chem., Anal. Ed. **13**, 1 (1941).

[4] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

compensated thermocouple* at the other focus.

Rays which pass through a prism at an angle to the horizontal are more strongly deviated than those which pass along the horizontal plane; this causes the image of the slit to be curved.[5] The curvature is a function of the refractive index of the prism for the particular ray but a calculation shows that a considerable improvement in resolving power can be obtained by the use of a curved slit. Slit S_2 was curved to fit the image of the slit for rays passing through a prism of index of refraction 1.47.

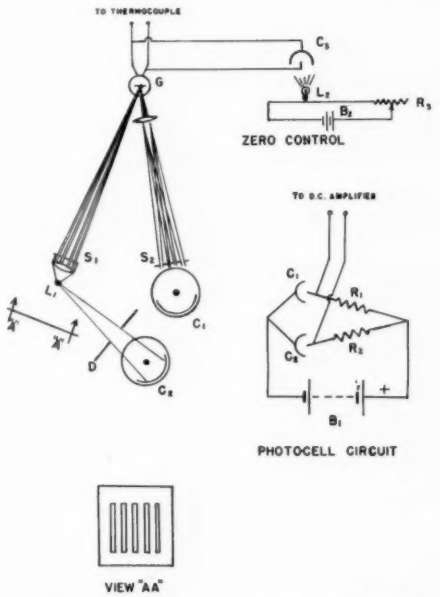
The table "T" holding the prism and Wadsworth mirror is mounted so that it may be moved in a vertical direction (Fig. 2). Four tables are provided, one above the other, upon which prisms of quartz, fluorite, rocksalt, and potassium bromide may be mounted. The prisms may be interchanged at will by means of a screw operating from the outside of the case.

The amplification system is shown in Fig. 3.

With no radiation striking the thermocouple, the diaphragm "D" is adjusted so that there is no potential difference between the anodes of the photo-cells C_1 and C_2. When infra-red radiation is allowed to strike the thermocouple, current from the thermocouple rotates the mirror of galvanometer G causing the image of the grid S_1 to be partially intercepted by S_2.[6] The light balance on the identical photoelectric cells C_1 and C_2 is thereby disturbed, and a potential is created. This is applied to a General Radio Type 815-A d.c. amplifier. Set for its highest sensitivity this instrument will amplify a current of 0.01 microampere to 5 milliamperes, a factor of 5×10^5. Since the thermocouple current may be as small as 10^{-11} ampere, the total amplification of the current from the thermocouple may be of the order of 10^9. The amplification can be varied, of course, by changing the brightness of the lamp L_1. The galvanometer and photo-cell amplifying system are mounted on a Mueller suspension.

Since temperature changes in the room cause the zero position of the galvanometer to change slowly it is necessary to provide a means of resetting the galvanometer to the position where the light striking photo-cells C_1 and C_2 is the same. (The actual movement of the reflected image from the galvanometer even with fairly large temperature variations is not more than a few tenths of a millimeter.) Since mechanical resetting of the mirror position is impractical, it is necessary to provide a means whereby an extremely small current (of the order of 10^{-10} ampere) may be applied to the galvanometer. A variable current of the right magnitude is produced by the arrangement shown in Fig. 3 labeled "zero control." This method of control of the zero of the primary galvanometer is thought to be novel. It is superior to the potentiometer commonly employed, because contact potentials and thermal e.m.f.'s do not affect the current in the control circuit.

The output current of the d.c. amplifier is applied to an Esterline-Angus 5 m.a. recorder. Spectra are traced directly on paper, thereby eliminating the loss of time in other spectrometers, where photographic records are obtained.



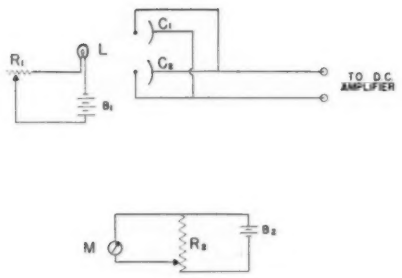
G—galvanometer (Moll)
R_1, R_2—10-megohm fixed resistors
R_3—60-ohm variable resistance
L_1—32-cp automobile headlight lamp
B_1—22½-volt "B" battery
B_2—6-volt storage battery
S_1, S_2—slotted brass plates
D—diaphragm
C_1 C_2, C_3—photoelectric cells. Type 917
L_2—3-volt flashlight lamp

FIG. 3. Amplifying system.

* Constructed by Dr. C. H. Cartwright.

[5] H. Hartinger, Geiger-Scheel, *Handbuch der Physik* (1927), Vol. 18, p. 236.

[6] Barnes, Brattain, and Seitz, Phys. Rev. **48**, 582 (1935). See also reference 3.



B_1, B_2—4-volt and 6-volt storage batteries
C_1, C_2—Type 917 photo-cells
R_1—60-ohm variable resistance
R_2—1000-ohm potentiometer
L—6-8-volt pilot lamp
M—Esterline-Angus 5-milliampere recorder

FIG. 4. Gain control.

The Esterline-Angus recording milliammeter has been equipped with a special pen to give a straight-line record. This recorder is very rapid in operation, one-third second being required for full scale deflection. Recorders which use a motor-driven pen generally have a period of five to ten seconds.

A new method of recording infra-red spectra has been developed by means of which the curves drawn by the spectrometer show directly the percentage transmission of a substance as a function of the position of the prism table. The operation is as follows: With the null cell in position, the zero and total intensity are adjusted (by varying the zero position and slit width) to correspond to 0 and 100 percent on some convenient scale. The prism table is then started rotating in the usual manner. The reading of the Esterline-Angus recorder is maintained at a constant value by manually turning a dial which controls the gain of the amplifier. On the same shaft with the "gain-control" is a potentiometer which is connected to a second Esterline-Angus recorder. A variation in the gain of the amplifier is thus accompanied by a change in the current passing through the second recorder, so that the curve obtained from this recorder is a record of the changes in the setting of the amplifier. When the desired spectral region has been scanned with the null cell in place, the spectrometer and the charts of the two Esterline-Angus recorders are reset to their positions at the beginning of the run and the null cell is replaced by the filled cell. The run is then repeated, the "gain-control" being operated in this case so that the record on the second Esterline-Angus recorder is duplicated. The curve obtained on the first recorder gives then the percent transmission of the filled cell.

Some difficulty was encountered in the construction of the "gain-control" since a resistance was required that could be continuously varied from 1 to 100 megohms. The problem was solved by the use of two photo-cells in opposition as shown in Fig. 4. Using the proper combination of lamp and resistance R_1 any range of resistances from values exceeding 10^{12} ohms to as low as 10^5 ohms can easily be obtained by this set-up. The potentiometer used in conjunction with the second E. A. recorder is also shown in the diagram.

In Fig. 5 is shown a typical infra-red record obtained without the use of the "gain-control." The curve was recorded using normal pentane at a pressure of 300 millimeters and the wave-length range was from 9.1 to 10.3 mu. The upper curve measures the energy transmitted by the null cell; the bottom curve measures the energy transmitted by the filled cell. The points marked zero represent the meter reading when a shutter was placed in front of the light source at the beginning and end of the run. Determination of the percentage transmission at a given point on the curve requires measurement of the vertical distance of each of the two curves from the zero line, followed by a calculation of the ratio of the two distances. To obtain a curve showing the percentage transmission of a sample as a function of the wave-length, one must

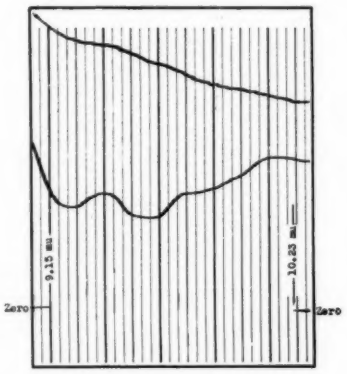


FIG. 5. *n*-pentane, 300 mm.

make these measurements at frequent intervals throughout the spectrum. Thus, to be sure that no bands in the spectral region presented in Fig. 5 were missed, about 60 measurements would be required.

Figure 6 shows the same spectral region as recorded using the gain control. All of the structure of the band is immediately obvious and the percentage transmission at any wave-length may be read directly.

The sensitivity and resolution of the spectrometer are both easily varied by changing the primary lamp voltage and the slit width or prism. The upper limit to the sensitivity of the instrument is set by the uncertainties unavoidably caused by Brownian motion of the galvanometer mirror. The resolution of the instrument is limited by the slit width and the dispersion and dimensions of the prism employed. In both cases the observed limiting conditions correspond closely to the theoretical values. Figure 7 compares records of the NH_3 10-mu band obtained by the present instrument and by Barker using a grating.

Other features of the instrument are: (1) A specially designed mounting for the collimating mirror which permits micro-adjustments to be made in the angle of rotation of the mirror about its axis, the height of the mirror, the tilt, the vertical and lateral displacement of the center with respect to the slit, and the distance from the slit so that very precise focusing is possible. See Fig. 2. (2) A variable ratchet arrangement for rotating the prism table which allows the angle through which the table is turned at each pull of the ratchet to be varied in integral amounts of 4×10^{-5} radian from 0 to 120×10^{-5} radian. The ratchet is operated by a synchronous motor which operates the ratchet at 3-second intervals. For rapid setting of the prism to any desired wave-length the ratchet may be disengaged and the prism table driven through a gear that rotates the table rapidly.

The spectrometer is calibrated by mapping the positions of known absorption bands such as those of NH_3, CO_2, etc. To protect the prism, to eliminate convection currents of air, and to remove water vapor, the instrument is enclosed in a tight, thermally insulated box, dried with potassium hydroxide and "dehydrite."

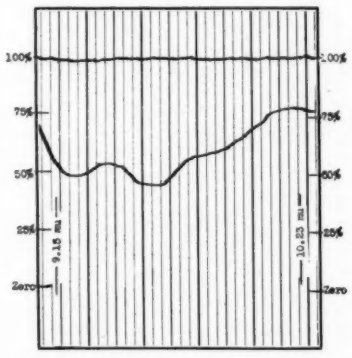


FIG. 6. *n*-pentane, 300 mm.

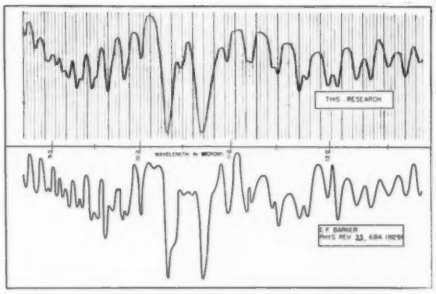


FIG. 7. Ammonia, 600 mm Hg press.

ANALYTICAL

Wright has given a good account of the types of analytical problems that may be solved by the use of infra-red spectroscopy. They may be classified as:

(1) Identification of unknown compounds.
(2) Detection of impurities.
(3) Quantitative analysis of mixtures.

Since the positions of the absorption bands in a compound can be predicted only roughly by theory, spectra prepared from pure compounds are prerequisite to any analysis by infra-red. Thus, an unknown can be identified only if it is known to be one of a group of compounds, whose spectra are available. Analysis of a mixture is possible if the spectra of the components of the mixture can be compared with the spectrum of the unknown. Quantitative analysis requires working curves which give the relation

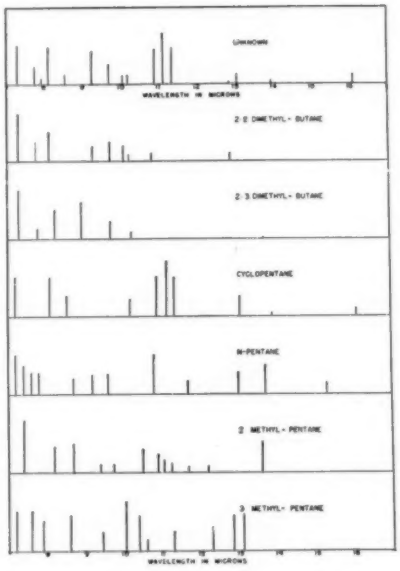


FIG. 8. Comparison of unknown and known spectra.

between the intensity of the absorption and the concentration of the substance being determined This relation is given very nearly by the Lambert-Beer's law, but deviations from the law are to be expected, particularly if gaseous samples are employed. The need for standard samples is, of course, not confined to infra-red analysis.

As an example of the first two problems we may mention a determination of the composition of a "cyclopentane cut" obtained in the distillation of a sample of natural gasoline. Spectra of cyclopentane and the other hydrocarbons boiling in the same range were available, hence all that was required was a comparison of the spectrum of the unknown with those of the various hydrocarbons. A comparison of this sort is most conveniently made by first listing the positions of all the bands of the mixture with an estimate of their intensity. Then, referring to similar lists of the bands of the suspected impurities, one checks all of the coincidences between the unknown and the comparison spectra. Finally by use of the rule that if a given band of a compound is observed, all stronger bands of the same compound must be present one can very quickly pick out the impurities (Fig. 8). It is evident that 2.2 dimethyl-butane is the only impurity present in a significant amount. The time required for this analysis was 45 minutes. Analysis by chemical and other physical methods had been abandoned as hopeless.

The infra-red method has been used for the quantitative analysis of mixtures containing as many as four hydrocarbons. The procedure is similar to that described by Wright.[3] A detailed discussion of quantitative analysis is reserved for a later publication.

I wish to acknowledge my indebtedness to Dr. Harold Gershinowitz for many helpful discussions. Mr. D. W. Mann and Mr. W. A. Ruska constructed the mechanical parts of the spectrometer using only rough sketches and verbal descriptions. Drs. O. Beeck and R. R. Brattain of Shell Development Company have been engaged in infra-red analysis of petroleum fractions and I have profited by their experience. Professor E. Bright Wilson, Jr. generously contributed much to the design of the spectrometer through his interest and advice. I have been ably assisted in the experimental work by Mr. E. S. Corner and Mr. C. F. Ellis.

A New Microphotometer*

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IN the design of a microphotometer, the problem which the authors have attempted to solve is simpler in two important respects than that undertaken by the manufacturer of instruments for general distribution. The instrument was intended, not for general use, but rather for a specific routine the details of which were thoroughly known beforehand from their development; it has appeared advantageous to omit certain adjustments recommended[2] for more diverse use. Further, the application was such that the desirability of continuous reliability and freedom from interruptions for maintenance service far overshadowed in importance any considerations of minimizing the initial cost. While the instrument may not, without modification, meet all spectrochemical requirements of cost and versatility, it is thought that some of its novel features may be of interest.

In the discussion of the instrument, it has appeared desirable to review in turn the major requirements for the indicating, photoelectric and optical systems, and for the lamp and the mechanical arrangement followed by a description of the interpretation of these requirements in terms of an operating photometer.

In the design of a spotting microphotometer for rapid routine service, careful attention should be given to the indicating system. While the instrument readings may be recorded through the use of any of a variety of types of automatic recorder, such procedure appears to offer, for the measurement of pre-selected non-consecutive lines, small possibility of improvement of speed, reliability or convenience beyond that attainable with indicating equipment. Hence consideration will be given to apparatus adapted for direct scale reading only.

If it is to be possible for the operator to maintain a measurement speed of 5 or 6 lines per minute, it is important, if not imperative, to make the reading of the instrument scale convenient. It appears probable that the most satisfactory indicating mechanism is realized through the use of a galvanometer and the projection of a moving cross-hair image on a fixed translucent scale. The scale should, preferably, be located near eye level and should be of such length that a least count of one-half millimeter provides adequate accuracy. Objections from a standpoint of increased fatigue are obvious for devices using a short scale, and hence, a small least count, as well as for those where readings must be made from a specific position due to parallax or other reason and for indicating meters which must be read with a head position other than erect.

The galvanometer used must, of course, have a suitably short period, say two seconds, and, hence, a rather low sensitivity; the question of the insertion of an amplifier between it and the photo-sensitive element arises. It must be recognized that additional complexity increases the hazard of service interruption for maintenance and that the successful use of an amplifier in close proximity to the powerful condensed spark previously described[3,4] is most difficult. It appears preferable, then, to build an instrument without an amplifier.

The omission of vacuum tube devices presupposes the use of a barrier-layer photovoltaic cell. Tests on a number of different types of such photo-cells have shown none which are ideal; all produced readings which depended in some measure on the past illumination history. However, with sufficient care in the arrangement of the operating procedure, one type, and perhaps others, may be adjusted to provide satisfactory reproducibility and good linearity in the relation-

* Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 21–23, 1941.

[1] The development reported was carried out in the Department of Physics in connection with industrial research projects sponsored through the Department of Engineering Research.

[2] R. A. Sawyer and H. B. Vincent, J. Opt. Soc. Am. **31**, 47, 1941.

[3] H. B. Vincent and R. A. Sawyer, J. App. Phys. **8**, 3 (1937).

[4] H. B. Vincent and R. A. Sawyer, Metal Progress **36**, 35 (1939).

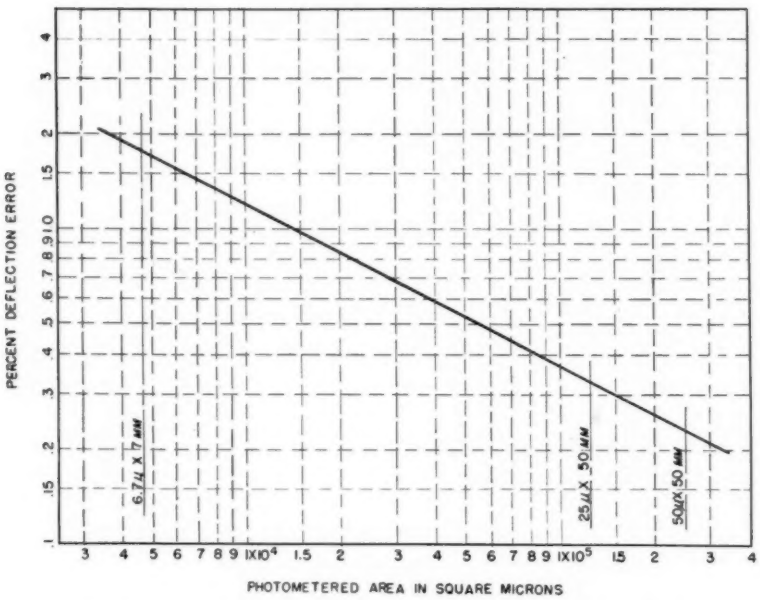

FIG. 1. The emulsion grain introduces an uncertainty which is related to the photometered area.

ship between incident intensity and galvanometer deflection.

A review of the indicating system chosen leads immediately to the conclusion that, even if the intensity of illumination of the plate is made very high, a fairly large area must be photometered to provide the energy necessary for a half-meter deflection at a reasonable galvanometer distance. However, the low sensitivity of the output system may not prove an insuperable handicap since, for independent reasons, it is desirable to photometer a large area anyway.

In an attempt to provide the highest analysis accuracy possible, due consideration must be given to the photographic errors and, in particular, to the statistical variation in the location of the silver grains. It may be shown quite readily from probability theory that, if the arrangement of the grains is random, the standard deviation to be expected in the galvanometer deflection is inversely proportional to the square root of the photometered area.

While the existence of statistical fluctuations cannot be doubted, they will be of interest only if their magnitude is such that they introduce important analytical errors. Figure 1 is a graph of experimental results obtained with the fine-grained photographic plates used for ferrous analysis, the coordinates being percent deflection error and photometered area in square microns. Since the grain error enters four times into the final results—once each for the element and matrix lines of both standard and test samples, it is apparent that significant grain errors may be anticipated unless an area of 10,000 to 15,000 square microns is used. If precision work is to be undertaken with photographic material of coarser grain the photometered area should, of course, be larger.

The illumination of the plate should meet two independent requirements. The low sensitivity of the indicating system chosen demands the highest possible intensity; at the same time, for convenience in spotting pre-selected lines on an unmarked plate, the projection of not less than a half-inch of the spectrum is desirable. A high intensity in the photometered area may be obtained by imaging a filament at the plate, but the projected area is then small. A consideration of the required area for a filament to produce similar intensity over the five by fifteen millimeter area to be projected leads to

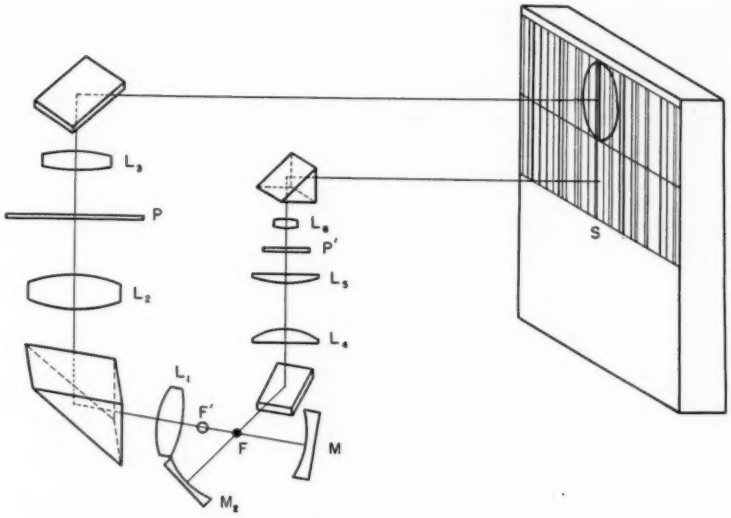

FIG. 2. The optical system.

serious problems in heat dissipation and input power control.

It is apparent, however, that the highest possible illumination need be provided for the measurement region only, and that a lower intensity is acceptable, and may, indeed, be preferable, for the remainder of the projected area. The optical design used to produce two different projection intensities is shown in Fig. 2.

The light from the filament F is imaged by the condensing lenses L_1 and L_2 at the plate P, and re-imaged, together with the spectrum on P at the screen S on the slit before the photo-cell.

A second beam, returning from the mirror M forms at F' an image which is re-imaged by L_1 and L_2 in the projection lens L_3. This beam illuminates at the plate an extent of 6/10 of an inch along the spectrum which is projected on the screen at a magnification of about eight diameters.

Arrangements have been made for the lamp to serve still another purpose. In foundry analysis, for all metals, elements and ranges, over fifty spectral lines are used, for steel, nearly a hundred; rapid recognition, without even occasional error, of all of these lines on an unmarked plate requires extensive training of the analyst. The projection of a reference spectrum bearing locating marks is of obvious assistance to the beginner. The images of test and reference spectra should be adjacent, should be at the same magnification and should move together.

Light from the filament F, reinforced by reflection from a curved mirror, M_2, illuminates, through the condensing lenses L_4 and L_5, the reference spectrum P' which is imaged at the screen S by the lens L_6. The two plane mirrors and the two prisms shown in the figure serve to direct the images to adjacent portions of the screen, a choice of suitable focal lengths for the lenses L_3 and L_6 provides a common magnification, while attachment of the two spectra to a single stage eliminates relative motion of the images.

For uniformity of line illumination and for good appearance of the screen image, a ribbon filament lamp would certainly be selected as an illuminant. However, tests on several samples of such lamps, supplied through the courtesy of Dr. W. E. Forsythe of the Nela Park Laboratories of the General Electric Company, indicated that, even if a brief useful life is accepted, the intensity produced is low.

Examination of the coil filaments which are available commercially led to the choice of a lamp having a close-wound helix rated at 8.5 volts, 4 amperes, T-8 bulb and single contact prefocus base. The small power consumption

minimizes the problems of heat dissipation and of regulation of the input voltage. The adequacy of the light emitted will be discussed in connection with the final tests.

The mechanical requirements of a microphotometer are concerned principally with rigidity, ease of manipulation and durability of the moving parts. In production control, the total load may exceed a million readings per year; operation over a period of several years with a minimum of maintenance should be provided. The location of the plate between the condensing and projecting lenses must be held for all plate positions within a small tolerance which decreases with increasing lens aperture; both rigidity and initial alignment must be adequate. Ease of operation is closely related to fatigue, which in turn reflects on operator accuracy and speed of output; it has a demonstrable financial value. Among important features may be mentioned simplicity and accessibility of controls. Delicate parts and adjustments should be avoided wherever possible; it should be virtually impossible to injure the instrument through error of manipulation of the controls.

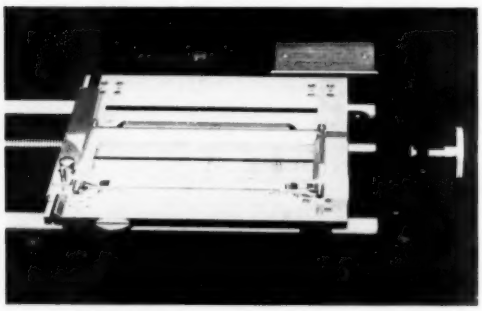

FIG. 3. The cross-slide.

Some of the structural details of the instrument constructed may be of interest. The base, a 200-pound casting 24 inches by 26 inches, carries through end supports two $1\frac{1}{4}$-inch stainless steel rods, Fig. 3. One of the rods carries a rack to which reference is made below. A rectangular aperture in the base is designed for the reception of the illuminating system.

The stage is carried on four roller-bearing supports adapted for motion along the rods. The rollers are used, not only to decrease the friction, but also to minimize the grinding action of abrasive dust, such as particles from plaster, which may find its way into the instrument. The pinion and driving wheel are engaged with the rack. A rear slot is provided for projection of the reference spectrum while the test spectrum receives its illumination through the forward slot.

For traverse of the spectral line across the point of measurement, a handwheel, through a train of hardened steel spiral gears, drives a worm at a speed reduction of five to one. The worm passes between two worm wheels which are attached to the stage. The worm wheels are free to rotate except for a frictional load which is imposed through fiber disks and an adjustable spring. The spring is set at such tension that the stage is carried along the thread of the worm without rotation of the worm wheels which form, however, a rolling nut permitting motion of the stage under a small frictional load.

The provisions for three stage motions are now apparent, *viz.*, a sliding motion for approximate positioning of the pre-selected line, a rack and pinion motion, operated by the left thumb, for close positioning and a geared motion for line traverse.

To ensure durability, all rotating shafts, including the pinion engaging the rack, are carried on ball bearings. The $2\frac{1}{2}$-inch handwheel is carried on a half-inch shaft; care has been taken to locate it far enough back on the instrument so that the operator's arm may rest comfortably on the table which supports the microphotometer.

To provide motion from one test spectrum to the next, the stage carries a cross-slide supported on a vee way at one end and on a steel ball at the other. The arrangement is shown in Fig. 3. The photographic plate is clamped in position by a spring-loaded rectangular ring. For the insertion and removal of plates, the ring is lifted by cams; the ejecting cam, at the left, aids in removal of the plate.

The reference spectrum is carried on a slotted Bakelite member which is inserted in a slide located beneath the stage; any number of reference spectra may be introduced in turn.

The illuminating and condensing systems are enclosed in a rectangular box inserted in an aperture provided in the instrument base. This

box houses the 34-watt lamp in an adjustable mounting, the concave mirror, the first condensing lens of f:2 aperture, the totally reflecting prism, with aluminized slant face, and the second condensing lens of f:1.5 aperture. This train provides illumination for the test spectrum. A small knob in front of the lamp mount permits adjustment of the aperture of the first condensing lens for sensitivity control. Light from the lamp and second concave mirror is directed by a flat

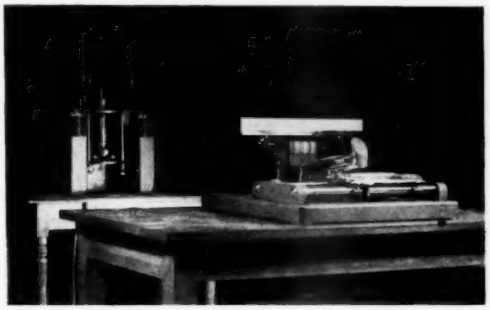

FIG. 4. The mounting of the optical system and the microphotometer completely assembled.

mirror through a condensing system for projection of the reference spectrum. The arrangement of the supports for the two projection lenses is shown in Fig. 4. The four half-inch rods attached to the base behind the stage provide good rigidity. While bracing from the front would be feasible, it is thought that the protrusion of the supports toward the operator has some undesirable features.

The screen arrangement is also shown in Fig. 4. The image of the reference spectrum lies below that of the test spectrum which, in turn, lies below the galvanometer scale. Operation demands little accommodation of vision for either direction or distance.

By means of the arm extending to the right of the screen, the photo-cell slit may be aligned with the line image. No locking mechanism is provided, but a frictional load is imposed on the motion to prevent fortuitous slippage. For maintenance of the galvanometer reading at complete opacity, the scale may be moved plus or minus three centimeters on a dovetail slide; the iris control mentioned above permits adjustment of the clear-plate or no-plate reading.

A simple optical system located behind the screen projects a cross-hair image which is focused on the scale after reflection from the mirror of a galvanometer mounted on a Julius suspension. A galvanometer-scale distance of two meters is used to keep the obliquity error for a straight scale within reasonable limits.

Tests of the instrument after assembly have established the following data. With the condenser iris set for 80 percent sensitivity to permit adjustment in either direction, a lamp voltage of 7 volts produces an opaque to no-plate deflection of 50 cm. Since the lamp is rated at 8.5 volts, a very slow blackening rate is anticipated. One hundred repeat readings taken on the same line at a galvanometer deflection of 32 cm showed that the probable error of a single observation amounts to less than 0.1 mm. Relative deflections for a line pair, with removal and readjustment of the plate between readings, showed a probable error in the deflection difference not exceeding 0.1 mm.

The rigidity, accuracy and ease of operation are thought to be acceptable, and satisfactory routine service is anticipated.

It is a pleasure to acknowledge the support of this development by the Ford Motor Company and the Bethlehem Steel Company. The design was prepared originally for the Ford Motor Company who have built, in their Rouge shops, an instrument for use in their open-hearth spectrochemical laboratory. The data and illustrations are taken from a microphotometer constructed at the University of Michigan for the Bethlehem Steel Company for use in their plant at Bethlehem, Pennsylvania.

Applications of the Spectrograph to Toxicological Investigations*

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New York State Police

INTRODUCTION

THE spectrograph has long proved its value in forensic investigations of bullet traces, paint analysis, etc. We have seriously doubted, however, its applicability to the study of metallic traces where much organic material was present, i.e., its application to toxicological investigations.

Perusal of the literature found it rather meager so far as any work in English was concerned. Even in the German publications, most investigators followed the pioneer methods of Gerlach[1] and concerned themselves with thallium, whose spectrum sensitivity is well known.

A brief review of toxicological literature involving the spectrograph is not amiss here. The writer first consulted Meggers and Scribner's *Index to the Literature on Spectrochemical Analysis*,[2] and the Van Someren *Spectrochemical Abstracts*,[3] as well as the standard works on toxicology such as Webster,[4] McNally,[5] and Gonzales, Vance, and Helpern.[6] It was found that poisoning due to thallium usually involved the use of rat poison composed of thallium sulphate with a fatty acid base, mentioned by Ritterskamp,[7] Van Calker,[8] R. Berge and H. P. Patzsch,[9] G. Schrader and O. Wiegand,[10] Schneller,[11] Gerlach, Rollwagen, and Intonti.[12]

A case involving thallium poisoning occurred in this country recently, in which five deaths resulted in a family of seven taken ill.[13] In the analysis, approximately 0.15 gram of each necropsy specimen was burned on high purity graphite electrodes in a 110-volt, d.c. arc operating at five amperes. Thallium was found in many body parts.

Gerlach,[1] Van Calker,[8] G. Schrader and O. Wiegand,[10] mention cases where arsenic was found, but no quantitative results are given. The high frequency spark method is usually employed.

METHOD

We use the spectrograph both as an analytical and as a survey instrument. Toxicological analysis for alkaloids is a long and tedious process but, nevertheless, one that must be carried out. Use is made of Autenrieth's modification of the Stas-Otto method, which depends upon the conversion of alkaloids into tartrates and the subsequent liberation with ammonia or other bases or acids. The alkaloids thus liberated are separated by the use of many solvents immiscible with water, such as ether, chloroform, and others. The solvent extracts are evaporated and the acid and basic residues are further purified by redissolving in dilute hydrochloric acid, filtering and extracting the filtrate as before. To these filtrates specific alkaloidal tests are applied.

In order to corroborate the chemical findings as much as possible in all toxicological analyses, we prepare each sample of the various organs by the Hess-Owens[14] method. In this procedure 0.4-g samples of test material are treated in a 30-ml Kjeldahl flask with 1 ml of concentrated sulphuric acid and heated on a sand bath heated with gas burners. When charring is complete,

* Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 21–23, 1941.

[1] W. Gerlach and W. Gerlach, *Chemical and Pathological Applications of Spectrum Analysis* (Adam Hilger, London, 1934).

[2] W. F. Meggers and B. F. Scribner, *Index to the Literature on Spectrochemical Analysis* (American Society for Testing Materials, 1939).

[3] E. H. S. van Someren, *Spectrochemical Abstracts* (Adam Hilger, London, 1941), Vol. II.

[4] R. W. Webster, *Legal Medicine and Toxicology* (W. B. Saunders Company, Philadelphia, 1930).

[5] W. D. McNally, *Toxicology* (Industrial Medicine, Chicago, 1937).

[6] T. A. Gonzales, M. Vance and M. Helpern, *Legal Medicine and Toxicology* (D. Appleton-Century, New York, 1940).

[7] P. Ritterskamp, Samml. Vergiftungsfällen **7**, 201–204 (1936).

[8] J. van Calker, Arch. f. Gewerbepathologie und Gewerbehygiene **7**, 685–91 (1937).

[9] R. Berge and H. Patzsch, Deut. tiertärtzl. Wochs. **43**, 20–21 (1935).

[10] G. Schrader and O. Wiegand, Samml. Vergiftungsfällen **7**, 135–138 (1936).

[11] J. Schneller, Deut. Zeits. ges. gericht. Med. **25**, 223–30 (1935).

[12] W. Gerlach, W. Rollwagen, and R. Intonti, Virchow's Arch. **301**, 588–601 (1938).

[13] J. B. Neal, E. Appelbaum, E. Gaul, and R. J. Masselink, N. Y. State J. Med. **35**, 657–659 (1935).

[14] T. M. Hess, J. S. Owens and L. G. Reinhardt, Ind. Eng. Chem. Anal. Ed. **11**, 646 (1939).

nitric acid is added until the solution becomes water clear, denoting complete oxidation. If the sample is particularly difficult to oxidize, a few tenths milliliter of concentrated perchloric acid is added. The solution is then evaporated to dryness and, when cooled, one ml of concentrated nitric acid added. Evaporation almost to dryness next takes place, care being taken not to over-heat the mixture. The residue is taken up in 0.4 ml of a 2*N* nitric acid solution containing the spectroscopic buffer and the internal control elements.

Of course, if we obtain negative results in the form of no metallic elements present, this does not indicate the absence of alkaloids—on the other hand, traces of the toxic metallic elements, if found, will direct further analysis and will confirm the chemist's findings.

Apparatus

Chiefly because of its conservation of material we have employed the condensed spark as a means of excitation. However, since quantitative results are sometimes needed, we have modified our original apparatus by using a Feussner[15] circuit. A transformer of 15,000 peak voltage charges a condenser which discharges through a series network comprising a synchronous interrupter, a resistor, and inductance and the sample gap. Their constants are as follows: Condenser, 0.005 μf; inductance, 500 microhenrys; resistance, 0.5 ohm; interrupter, a 3600 r.p.m. G.E. synchronous motor. It was found necessary to use the value of the inductance given in order to make the 3176.5 spark line of lead disappear completely. A variable resistance of 100 ohms is in series with the primary of the transformer, which allows a variation in the r.f. current usually kept constant at 2 amperes. This resistance also sharpens the point at which the r.f. circuit is synchronized to peak voltage.

Arsenic

On December 1, 1940, an elderly farmer in New York State died under what appeared to be normal circumstances. However, soon after his death, rumors were circulated to the effect that his wife had poisoned him. Needless to say these rumors found their way to the ears of the State Police, and in order to satisfy themselves as well as stop the ugly rumors, criminal investigation was started. Six weeks after burial the body was exhumed, and the organs, samples of embalming fluid, and soil from the top of the grave were sent to the laboratory. One-half gram samples of the liver, stomach wall, and stomach contents were acid digested as outlined previously. Meanwhile, our chemists found strong evidence of arsenic in preliminary Reinsch test.[16] In this test the organic material is finely ground and cooked with dilute hydrochloric acid in which a small piece of arsenic-free copper strip has been placed. Antimony, arsenic and mercury, if present, form a coating on the copper strip. To make the test more specific, sublimation of the deposit is performed; the coated copper is placed in a glass reduction tube sealed at one end, and the tube heated and then examined under a microscope. Characteristic globules will appear if mercury is present, or, as in this case, examination of the tube showed crystals of arsenic trioxide sublimate. If arsenic be present in the form of arsenates, a deposit will form readily; however, if pentavalent arsenic is suspected, it is wise to treat the material under investigation with a little sodium sulphite to reduce the arsenic to the arsenous (trivalent) form; or one may add a few crystals of ferrous sulphate, and the coating on the copper will appear in a short time.[4] However, no lines of arsenic were found in the spectrograms of the ashed samples. The Gutzeit[17] test, a modification of the classical Marsh[18] test, for arsenic was then performed, and the quantity of arsenic present was found to be of the order of 150 to 190 milligrams per kilo, a result confirmed independently by the Bender Laboratories of Albany, New York.

Since, theoretically, the copper in the Reinsch test is coated with an alloy of arsenic and copper, a new Reinsch sample was prepared and the coated copper spectrographed directly in the d.c. arc. The result is shown in Fig. 1. Sample number 1 is arsenic trioxide, reagent grade; sample number 2 the Reinsch copper coated with the

[15] O. Feussner, "Technic of spectrographic analysis," Arch. f. Eisenhuttenwes. **6**, 551 (1933).

[16] J. f. prakt. Chemie **24**, 244 (1841).

[17] Pharm. Ztg. **24**, 263 (1879).

[18] London Med. Gaz. **18**, 650 (1836).

FIG. 1.

arsenic from the liver sample; and sample number 3 a copper sample known to contain, by previous chemical analysis, 0.0018 percent arsenic. The copper used in the Reinsch test had been previously shown to be spectrographically free from arsenic.

Various estimates are given in the literature as to the lowest concentration of arsenic that may be detected spectrographically. These range from 0.03 percent[19] to 0.001 percent.[20] The latter range would amount to 10 milligrams per kilo, which is the amount usually found in the hair and bones in arsenic poisoning cases, and nowhere near the gross amount found in the liver and other organs, which may amount to better than 200 milligrams per kilo.

Field investigation proved that this was not a case of homicide but rather suicide; the method was arsenic poisoning.

LEAD

The greater sensitivity of the spectrograph to lead in comparison with arsenic was shown in a recent case involving the malicious poisoning of a valuable cow. The liver was sent to the laboratory some two weeks after removal. A sample was ashed in the usual manner and a spectrographic analysis was undertaken of this, as well as of some suspected powder. Lead showed up clearly in the spectrogram of the ashed sample, but only in the powder was there any indication of both arsenic and lead. Once again the Reinsch test was applied and the arsenic coated copper strip burned completely in the d.c. arc. The arsenic lines 2288 and 2349 now appeared. The powder was found to contain lead arsenate to which sodium chloride had been added, probably to serve as a "salt lick."

The detection of lead in whole blood can be done directly. A few drops of blood are dried in the electrode which should be spectrographically pure graphite. In a case in question, two men, painters, showed many evidences of lead poisoning. However, neither patient was found to give evidence of basophilic stippling of the blood cells, which is characteristic, although not specific, evidence of lead poisoning in chronic cases. Definite evidence of lead however was found spectrographically. This investigation was not of a criminal nature, but merely to aid the physicians of a local hospital in their diagnosis.

BARIUM

In a previous paper [21] the writer mentioned a case of animal poisoning in which barium was readily detected by ashing the meat directly in the spectrographic arc. This poison is rare in spite of the number of "barium meals" given for fluoroscopic and x-ray studies.

PHOSPHORUS

Since organic phosphorus is invariably present in the intestinal contents, its spectrographic determination must be based on the increased density of the phosphorus lines if the element is present in excess. In one case analyzed candy fudge was so impregnated with yellow phosphorus that, when the heart-shaped Valentine candy box was opened, the characteristic garlic odor was unmistakable. Phosphorus is sometimes partially oxidized *in vivo*. A six-year-old child of poor circumstances ate some refuse from a dump heap where she had been playing with other children. The child was taken violently

[19] D. M. Smith, *Metallurgical Analysis by the Spectrograph* (British Non-Ferrous Metals Research Association, 1933), p. 94.

[20] E. K. Jaycox and E. A. Ruehle, *Proceedings of the Seventh Conference on Spectroscopy* (John Wiley and Sons, New York, 1940), p. 12.

[21] C. W. Rankin, *Proceedings of the Sixth Spectroscopy Conference* (John Wiley and Sons, New York, 1939).

ill that evening and died early next morning. The vomitus when ashed and spectrographed showed much phosphorus present. The stomach contents and the intestines gave only a faint reaction.

Mercury

For the detection of mercury we have found that best results are secured by using a gaseous discharge tube illustrated in Fig. 2. This tube was designed from one used by Pfeilsticker[22] for the determination of certain halogens. The organic matter is destroyed by the method already outlined,[14] and then the lower copper electrode of the tube is dipped for about one-half inch in the concentrated solution and connected to the positive side of a battery, the negative pole of which is connected to a spiral platinum anode. Within five minutes all of the mercury will be deposited on the electrode, which is then placed in the discharge tube, the pump is then started until the pressure in the tube is from 10 to 25 mm of Hg. The tube is excited with the Feussner condensed spark arrangement previously described.

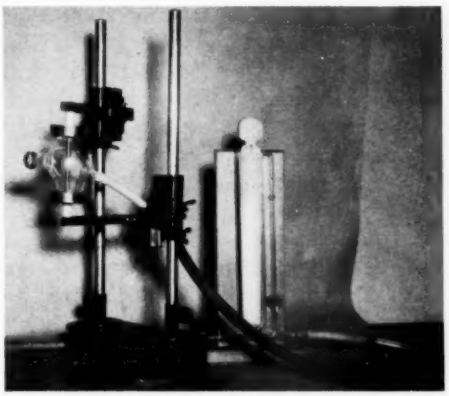

Fig. 2.

[22] K. Pfeilsticker, "Spektralanalyse der Halogene und anderer schwer anregbarer Nichmetalle," Spectroch. Acta 1, 424–36 (1940).

With such a set-up the mercury line 2536.5A is present with test solutions of mercury of 1 part in 100,000,000. When the mercury is present in toxic quantities 4358.3; 3554; 3650.1; 2847.7, and 2536.5 all are present.

Conclusion

In conclusion, it is important to note that in scientific criminal investigation one cannot follow any standardized spectrographic analysis. Evidences submitted for spectrographic analysis will vary from one-half cc of blood to a four-pound liver, sometimes in good condition, more often badly decomposed. We rarely get *pure* samples—contamination is a big factor whether it be in the form of embalming fluid or in cases of animal poisoning—pieces of grain, hay, soil, etc. When vomitus is scraped from the ground or recovered in a feed box, we usually have about 90 percent contamination and 10 percent sample. Under these circumstances, we cannot follow any definite procedure, and each case, therefore, receives slightly different treatment. We do not know what limitation can be placed upon the spectrograph since literature does not reveal much recent research on criminal investigation. However, it is our sincere belief that, in the near future, the spectrograph will be used for toxicological analysis in criminal investigations to reveal traces of the halogens, alkaloids, etc.

Naming Spectroscopic Analytical Methods*

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THE possibility of employing the spectroscope as an instrument of chemical analysis, both qualitative and quantitative, has been realized since the time of Alter. Recent years have brought a greatly increased interest, both by physicists and chemists, in this analytical tool.

Current literature on analytical applications of spectroscopy seems confused in the usage of terms. Presumably this may be attributed (1) to analysts' failure to adopt a comprehensive classification of all types of analytical methods, and (2) to physicists' apparent lack of familiarity with these methods. The object of this paper is to consider the cause of the confusion and to suggest a possible nomenclature for use.

THE PROBLEM OF NAMING METHODS

It is desirable to name each kind of analytical method in order that we may communicate with each other concerning them. The name adopted should be as appropriate, specific, and concise as possible, and, in addition, it should conform to the generally approved scheme of nomenclature in use. Unfortunately, analysts have not agreed upon a consistent nomenclature sufficiently adaptable and comprehensive to include the wide variety of methods known. Among the named procedures now in use many are designated by the name of the originator, by the kind of material to which they are adapted, or by the nature of the technique employed.

Naming in terms of the technique seems preferable, in order to convey an idea of what is done in the method. In this case one must consider the possibility of indicating several general operations. Those involving selection, preparation, and measurement of the sample are so nearly universal that no mention is made of them. The next one, if it is encountered, is the preliminary treatment, which may include one or more of the following processes: fusion; dissolution; adjustment of certain factors causing variation, such as *p*H or the state of oxidation; and accomplishment of certain transformations necessary for the succeeding operation. In spectroscopy, the last process often includes the production of a suitable colored absorbing system or the volatilization of the material. In naming methods, analysts ordinarily make no attempt to indicate the nature of any such treatment.

The next operation, if necessary, is the separation of the desired constituent from any interfering constituents present. The commonly used processes are volatilization, precipitation, electrodeposition, and extraction. These operations are so important in their possible effects upon the reliability of the final results that some effort has been made to have the name of a method indicate the general nature of the process of separation used.

The final operation, measurement of the desired constituent, is the most important, since the determination of the amount of this constituent is the objective of all quantitative analyses. Every method, if named on the basis of the nature of the analytical procedure involved, should indicate the method of measurement in order to convey desired information to those concerned. Present operational nomenclature does indicate the kind of measurement in many cases; but practice, even among analysts, is neither as inclusive nor consistent as desirable.

To indicate the method of measurement, it seems best to name the procedure according to the property measured, such as mass, volume, pressure, density, color, and others. Three suffixes are available: -meter, to denote an instrument for measuring the quantity; -metry, to denote the kind of measurement; and -metric, to use as the adjectival form for kind of measurement. Then we have, for example, colorimeter, colorimetry, and colorimetric. By using the adjectival form with the appropriate word for

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the method of separation involved, we have a combination which meets the requirement of designating both the methods of measurement and of separation. Representative examples are gravimetric electrodeposition, titrimetric precipitation, manometric extraction, and colorimetric volatilization. Since proposing this system,[1] the author has used it successfully with large groups of students.[2]

Application to Procedures Employing Spectroscopes

Since a spectroscope, considered as an analytical tool, is an instrument of measurement,[3] and since one measures a property of the spectrum, it seems desirable to name methods based upon the use of this instrument to harmonize with other analytical procedures.

A number of terms, in addition to spectroscope itself, have been, or are being, used in the literature dealing with chemical analysis. Some of these, with a dictionary definition, follow: spectrum—the image formed when a beam of light is subjected to dispersion;[4] spectrum analysis—chemical analysis effected by investigation of spectra; spectroscopy—use of the spectroscope; spectrometer—a spectroscope fitted for measurement of the spectra observed with it; spectrometry—art or process of using a spectrometer; spectrograph—apparatus for photographing or mapping a spectrum; spectral—pertaining to a spectrum; spectroscopic—produced by a spectroscope; spectrophotometer—instrument for comparing intensities of corresponding colors of two spectra; spectrophotometry—use of a spectrophotometer.

The selection of appropriate terms for use in analytical spectroscopy should take into account what can be done with the instrument and how this is done. Thus, determinations of desired constituents may be either qualitative or quantitative, or both. The portion of the spectrum to be observed or measured is obtained by absorption or emission of radiant energy. Actinic, visual, or thermal properties of this energy are utilized in obtaining the analytical data, the particular one used depending upon the region of the spectrum involved. The general term would be radiometric, but more specific terms, such as photographic, visual, and photoelectric, are more likely to be encountered.

Current Usage

In referring, in general, to methods which use a spectroscope, it is obvious that any term employed should have a very broad meaning. Of the common terms, only spectrum analysis, and the adjectives spectroscopic and spectral, meet this requirement. None of them implies anything about how the information is obtained, nor whether it is qualitative or quantitative in nature. Spectrographic is more restricted in indicating a photographic procedure. Spectrophotometric refers to absorption measurements made by one of the 144 kinds of instruments that have been proposed as possibilities.[5] Even then the use of an ordinary spectroscope is not included.

Some usage has developed for which there does not seem to be adequate justification, an example being the term spectrochemical. Few analysts know just what is meant by this word. It implies the use of, or at least the possibility of using, related terms, such as densochemical or colorochemical, which we do not have. The ending -chemical has no reference to the method of measurement, since all of these are physical in nature, nor does it apparently have any reference to a method of separation. Since many materials require no preliminary treatment, it cannot refer to this operation; but in any case analysts do not name methods with this operation in mind. It would seem, therefore, to have no sound justification.

Suggested Usage

In view of long usage and appropriateness, it is probably desirable to continue the word spectroscopic in its most general sense for referring to procedures, either qualitative or

[1] M. G. Mellon and D. R. Mellon, J. Chem. Ed. **14**, 365 (1937).
[2] M. G. Mellon, *Methods of Quantitative Chemical Analysis* (Macmillan Company, 1937).
[3] More exactly, it provides the spectrum, a property of which is measured.
[4] Emission and absorption spectra are included here.
[5] Staff of the Institute of Paper Chemistry, Paper Trade J. **105**, No. 18, 135; No. 19, 27 (1937).

quantitative, which employ a spectroscope. Filter photometers should not be included. For quantitative methods, the general term spectrometric seems most appropriate. It might apply to qualitative measurements also if one considers that any such observations are referred ultimately, at least in the observer's mind, to some standard line or position. This word indicates that there is a measurement and that it involves the spectrum. Then, if necessary, any of the methods of separation used may be indicated by adding the appropriate word. If desired, the adjective absorptive or emissive may precede the word spectrometric. Then one might apply the designation "absorptive spectrometric precipitation" to Mehlig's method[6] for determining manganese.[7] The term spectrometric implies two others: spectrometer and spectrometry, the use of which is clear. Physicists have used the word spectrometer in a somewhat more limited sense, but this does not seem to agree with the definition quoted herewith.

[6] J. P. Mehlig, Ind. Eng. Chem. Anal. Ed. **7**, 27 (1935).

[7] In naming the method, it is probably undesirable to try to be more specific; but in an account of a research, as in articles in periodicals, writers should leave no uncertainty about the kind of apparatus used and the conditions of use. Thus, visual spectrophotometric observations, with a wide spectral band, may be seriously in error, especially in the red and violet regions.